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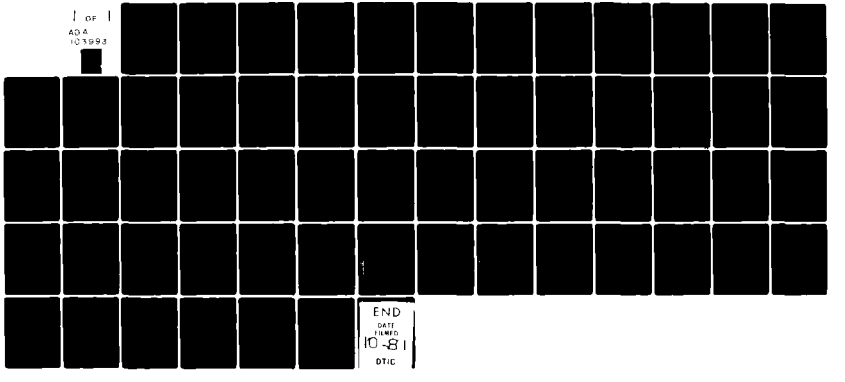

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The Electrogeneration of Solvated Metal Atoms. II.
Analyses of the stabilities of solvated cations and atoms.

by P. P. Schmidt
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Prepared for Publication in the
Electrochemica Acta

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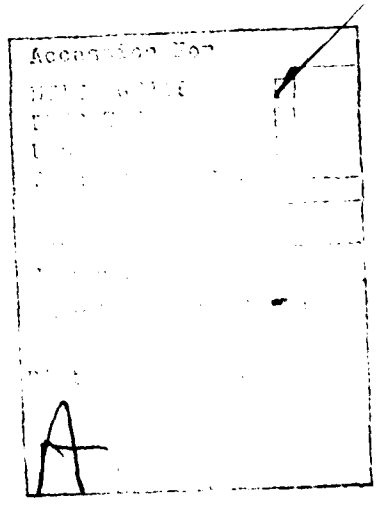

The Electrogeneration of Solvated Metal Atoms. II. Analyses of the stabilities of solvated cations and atoms

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Abstract

The purpose of this paper is to investigate mechanical models of ionic and atomic solvation in order to suggest a part of the mechanism of the electroreduction of metal ions. We use a Morse potential, the parameters for which are determined with the use of spectroscopic information, to try to predict the mechanical properties of a solvated atom. In particular, the solvated ionic and atomic systems are allowed to approach and interact with a metallic surface. Changes in the positions of the equilibria and changes in the calculated force constants are determined. We define accurate adionic and adatomic states. In these states the ion or atom occupies an expanded cage which includes the solvent and the surface of the metal. The activation energies for the formation of adions may be much larger than the activation energies for the formation of the related adatoms. Thus, if a reduction should occur at the outer Helmholtz plane, a solvated atom can be formed. In the vicinity of the surface, such a solvated atom can desolvate much more readily than the ion. The strength with which solvent or ligand is associated with a zero-valent metallic species, we believe, influences strongly the character of the metallic deposit formed.

1. Introduction

Although the electrodeposition of metals is important, our knowledge of the process at the molecular level nevertheless is rudimentary. Therefore, in an effort to try to understand better the events which occur during the course of the reduction of the ion and its deposition as a metal atom onto the surface of the electrode, we present the following analysis. In particular, we suggest that a possible route for the deposition of some metal atoms onto the surface depends upon the generation of free solvated atoms in the interface. These atoms subsequently desolvate to release the atom for bonding to the metal.

Of the forces which operate between the ion and its primary shell of solvent, the electrostatic attraction between the ion and the solvent dipoles is the strongest. Nevertheless, as we have recently shown,[1,2] the far infrared active vibrations of the ion inside a regular, crystalline cage of solvent yield information largely about the forces of repulsion and the van der Waals attractions which operate between the ion and the molecules of solvent. These forces can be modelled successfully with the use of several simple functions. It is possible then to account for the observed trends in vibrations of the various solvated ionic species.[1,2]

In addition, we also have predicted the vibrational maximum and line-shape for a simple solvated lithium atom.[3] Our prediction was based on the use of a correspondence between the form of the Born exponential repulsion and the Morse potential. Factors common to both potential energy functions were identified. The force

constant predicted for an atom interacting with a cage of solvent molecules through the forces of the Morse potential was then evaluated. We suggested the vibrational band maximum may be found in the range of 300-400 cm^{-1}.[3]

The analysis we carried out[3] enables us to define the form of the Morse potential which we intend to use in the analysis of the stability of the solvated atomic system, the subject of this paper.

It is important to note that although the electrostatic contribution to the vibrational force constant vanishes for the ion in a crystalline cage of solvent [by virtue of factors of symmetry], the electrostatic forces of attraction are still important in the solvated ionic system. For the consideration of the process of ionic desolvation, the electrostatic interactions should play a substantial role. As the ion, within its regular cage of solvent, is displaced beyond the limits of the harmonic restoring forces, the ion should begin to experience the effect of strong electrostatic attractions. In contrast, as a solvated atom is displaced beyone the limits of its harmonic restoring forces, the anharmonic forces for restoration may not be as great. Alternatively, the atom may be created, by the process of reduction, in a state of solvation which is intrinsically unstable. The ionic state may require an activated desolvation.

The strict desolvation of an ion may not always occur to produce a bare ion at the metal surface. The formation of such a surface-bound ion should involve a partial covalent bond between the ion and the surface. However, as shown later with reference to the lithium ion, even the formation of a partial covalent bond with the surface may not be incentive enough to induce desolvation.

On the other hand, if the reduction of a metal ion can occur

by means of an outer sphere mechanism somewhere in the vicinity of the outer Helmholtz plane, then the formation of a solvated atom is likely. The removal of the atom from its sheath of solvent is much easier to accomplish than is the removal of an ion.

The following sections present an analysis which builds upon the suggestion that the reduction of an ion to form a solvated atom is possible. No consideration is given to the problem of the determination of the theoretical rate constants for this process. Instead, at this time we explore the nature of the solvated atomic states as contrasted to the similar states for the ion. The objective is to determine how stable one system is compared to the other. This is done through the investigation of the stability of a system with respect to the displacement of the ion or atom along a vector which is directed from the centre of solvation through a planar face of the cage of solvent. At the other side of this plane is the metal surface. The effect of the metal will be approximated merely by one atom.

2. States of Solvation and the Vibrations of Solvated Ions and Atoms

A discussion of the far infrared active vibrations of the simple, solvated alkali metal cations has been given previously.[1-3] These particular states of vibration were examined in order to construct a potential energy function for the state of solvation of an ion. Here, we shall be concerned with the analyses of mechanical stability within the states of solvation for ions and atoms. It is sufficient therefore merely to summarize the formulae needed to proceed to the consideration of the stabilies of solvated ionic

and atomic systems.

In addition to listing the formulae needed in the subsequent analyses, we consider the character of the solvation of a free ion or metal atom. This examination is necessary in order to try accurately to estimate the form of the potential energy function for the solvated atom.

The experimental evidence[4] indicates that the far infrared spectra of simple, solvated ions are largely insensitive to the nature of the solvent. Shifts in the maxima for various solvents are of the order of a few wavenumbers. As a consequence, it is valid to interpret these vibrational maxima as arising from the vibrations of the metal ion within a cage of solvent molecules. The specific vibrations of the molecules, internally or about their centres-of-gravity, contribute very little to the spectrum.

The potential energy function for an ion or atom trapped within a complicated cage of sources can be determined with the use of pair-wise interactions. In order to consider harmonic oscillations of a centrally solvated ion or atom, or to consider questions of dynamic stability, it is necessary to determine the second order coefficients in a Taylor series expansion of the complete potential functions. For a system with a complicated distribution of sources, the vectorial Taylor series can be used. When appropriately handled, it is possible to develop expressions for force constants in a manner which is similar to the treatment of crystal field problems.[1,5-7]

For a scalar function of the form

$$g(\underset{\sim}{R}) = \sqrt{4\pi}Y_{00}(\hat{R})f(R) = f(R) \qquad (2.1)$$

in which $Y_{\ell m}$ is the spherical harmonic function,[9] the Taylor series is given by[5]

$$g(\underset{\sim}{R}+\underset{\sim}{r}) = \sum_{n=0}^{\infty}(r^n/n!)\sum_{\ell} A_{n\ell} P_\ell(\hat{R}\cdot\hat{r}) \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!} R^{-q}$$

$$\times\left(\frac{n-q}{R} + \frac{d}{dR}\right)\left(\frac{d}{dR}\right)^{n-q-1} f(R). \qquad (2.2)$$

Here,

$$A_{n\ell} = 0 \qquad \text{for } \ell > n \text{ and } n - \ell \text{ odd}$$

$$= \frac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!} \qquad \text{for } \ell \leq n \text{ and } n - \ell \text{ even} \qquad (2.3)$$

and $P_n(x)$ is the Legendre polynomial of order n. The quantity $\hat{R}\cdot\hat{r}$ is the scalar product of the unit vectors $\hat{R}$ and $\hat{r}$ where $\underset{\sim}{r}$ is the vectorial displacement about the end-point of the vector $\underset{\sim}{R}$.

The advantage of the formula (2.2), as we have discussed and illustrated elsewhere,[5-7] is the ease with which it can be applied to a number of problems. In particular, eq (2.2) separates angular and radial dependencies in the same manner as is done with the Laplace expansion of the Coulomb potential.

The first and second order terms are of particular interest to us. They are

$$t_1(\underset{\sim}{R}+\underset{\sim}{r}) = -rP_1(\hat{R}\cdot\hat{r})\frac{df}{dR} \qquad (2.4)$$

and

$$t_2(\underset{\sim}{R}+\underset{\sim}{r}) = \frac{1}{2}r^2\left[\frac{1}{3}\left[\frac{2}{R}\frac{df}{dR} + \frac{d^2f}{dR^2}\right] - \frac{2}{3}P_2(\hat{R}\cdot\hat{r})\left[\frac{1}{R}\frac{df}{dR} - \frac{d^2f}{dR^2}\right]\right]. \tag{2.5}$$

The specific first and second order Legendre polynomials are

$$P_1(x) = x \tag{2.6}$$

$$P_2(x) = \frac{1}{2}(3x^2-1). \tag{2.7}$$

The first order contribution to the Taylor series is easily converted into the usual form for the force acting on a test particle:

$$t_1(\underset{\sim}{R}+\underset{\sim}{r}) = \underset{\sim}{r}\cdot\underset{\sim}{F} \tag{2.8a}$$

$$\underset{\sim}{F} = -(\underset{\sim}{R}/R)\frac{df}{dR}\ . \tag{2.8b}$$

The second order term, when evaluated at a point where $\underset{\sim}{F} = 0$, yields the "force constant" for the harmonic oscillation of the test particle. If the evaluated "force constant" is negative, any motion at the point of vanishing force must be unstable. This familiar mechanical maxim will be essential to our analyses.

Given an individual pair potential $v(\underset{\sim}{R}_{ij})$, we assume the complete potential for a system of masses or charges to be pairwise additive. Thus,

$$V(\underset{\sim}{R}) = \sum{}' v(\underset{\sim}{R}_{ij}) \tag{2.9}$$

where the summation excludes self energies (i=j) and i>j. If one element, a centrally solvated ion or atom, for example, is common

to all of the pairs in the summation (2.9), then it is possible to consider the displacement of that particle vectorially in any direction away from the original location, $\underset{\sim}{R}$. Thus,

$$V(\underset{\sim}{R}+\underset{\sim}{r}) = \sum{}' v(\underset{\sim}{R}_{ij}+\underset{\sim}{r}) \tag{2.10}$$

and each $v(\underset{\sim}{R}_{ij})$ is given its own Taylor series (2.2) for a displacement $\underset{\sim}{r}$ with respect to $\underset{\sim}{R}_{ij}$.

In previous papers[1,2] we have investigated several potential energy functions which can be used to characterize the state of solvation of an ion. With the use of these functions, it is possible to obtain expressions for the force constants for the far infrared active vibrations. Thus, values of the parameters in the potential functions can be determined.

For the consideration of the stabilities of states of solvation of solvated atoms, in this paper we shall lay a particular emphasis on the use of the Morse potential. We do this here, not for reasons of the accuracy of the functional form (that accuracy has not been clearly demonstrated for these systems), but rather at this point the function yields results which are physically transparent. The results are more transparent than is the case with the use of other more complicated, and perhaps more numerically accurate, forms. Nevertheless, in this section we do provide a sketch of the behaviour of one more complicated functional form, the combination of an exponential repulsion and the ion-induced dipolar interaction.

Because the far infrared active vibrations of an ion inside a cage of solvent do not depend upon the vibrations of the solvent which make up the cage, it is necessary only to consider the

interactions between the ion (and subsequently the atom) and the solvent. That is, interactions between solvent dipoles may be neglected, especially with reference to questions of the stability of a centrally located species against small displacements. The obvious contributions to the interaction between the ion and the surrounding solvent, therefore, are the ionic-dipolar, ionic-induced dipolar, van der Waals (induced dipolar-dipolar), and overlap repulsive interactions. A combination of exponential potential functional forms yields the Morse potential. We now list the first and second terms in the Taylor series for these potential forms.

For a Born exponential repulsion,

$$\phi_B(\underset{\sim}{R}) = B \exp[(R_0-R)/\rho] \tag{2.11}$$

where B and ρ are constants, we find

$$t_{1B}(\underset{\sim}{R}+\underset{\sim}{r}) = \underset{\sim}{r}\cdot\underset{\sim}{R}\,\frac{B}{\rho R}\exp[(R_0-R)/\rho] \tag{2.12a}$$

with the force given by

$$\underset{\sim}{F}_B = \frac{B}{\rho R}\,\underset{\sim}{R}\exp[(R_0-R)/\rho]. \tag{2.12b}$$

The second order term is

$$t_{2B}(\underset{\sim}{R}+\underset{\sim}{r}) = \tfrac{1}{2}r^2\,\tfrac{1}{3}\,\frac{B}{\rho^2}\exp[(R_0-R)/\rho]\left[(1-2\rho/R) + 2P_2(\hat{R}\cdot\hat{r})(1+\rho/R)\right] \tag{2.13}$$

With the use of eq (2.7), this expression is easily converted into

a cartesian form. The cartesian form is useful for those cases of solvation in which the distribution of solvent ceases to be regular and crystalline. We write

$$t_{2B}(R+r) = \frac{1}{2}\underset{\sim}{r}\underset{\sim}{r}:\underset{\sim}{K}_B \tag{2.14}$$

in which K_B is a cartesian (force constant) matrix with elements given by

$$k_{Bxx} = \frac{B}{3(\rho R)^2}\exp[(R_0-R)/\rho]\left[(2X^2-Y^2-Z^2)(1+\rho/R) + R(R-2\rho)\right] \tag{2.15a}$$

$$k_{Bxy} = 2\frac{B}{(\rho R)^2}XY(1+\rho/R)\exp[(R_0-R)/\rho] \tag{2.15b}$$

with the remaining terms generated by permuting X, Y, and Z. The coordinates X, Y, and Z refer to the location of the molecular source of the Born repulsion.

The Morse potential is

$$\phi_M(\underset{\sim}{R}) = D\exp[a(R_0-R)]\left[\exp[a(R_0-R)] - 2\right]. \tag{2.16}$$

The first order term in the Taylor series is $t_{1M} = \underset{\sim}{r}\cdot\underset{\sim}{F}_M$ with

$$\underset{\sim}{F}_M = \frac{2aD}{R}\underset{\sim}{R}\exp[a(R_0-R)]\left[\exp[a(R_0-R)] - 1\right]. \tag{2.17}$$

The second order term is

$$t_{2M} = \frac{1}{2}r^2\, a^2D\,\frac{2}{3}\exp[a(R_0-R)]\left[2\exp[a(R_0-R)](1-1/aR) - 1 + 2/aR\right.$$

$$+ P_2(\hat{r}\cdot\hat{R})\left[4\ \exp[a(R_0-R)](1+1/2aR) - 2(1+1/aR)\right]\Big]. \qquad (2.18)$$

Cartesian elements for the second order expansion of the Morse potential are easily constructed from (2.15a) and (2.15b) etc.:

$$t_{2M} = \frac{1}{2}rr:K_M \qquad (2.19)$$

with

$$k_{Mxx} = \frac{a^2D}{3R^2}\exp[a(R_0-R)]\Big[(2X^2-Y^2-Z^2)\Big[4(1+1/2aR)\exp[a(R_0-R)] - 2(1+1/aR)\Big] + R(R-1/a)\exp[a(R_0-R)] - 2R(R-2/a)\Big] \qquad (2.20a)$$

and

$$k_{Mxy} = 4\,\frac{a^2D}{R^2}XY\exp[a(R_0-R)]\Big[2(1+1/2aR)\exp[a(R_0-R)] - R(R+1/a)\Big]. \qquad (2.20b)$$

The ionic-induced dipolar interaction is

$$\phi_{ID}(\underset{\sim}{R}) = -\frac{(Ze)^2\alpha_s}{2R^4} \qquad (2.21)$$

where α_s is the polarizability of the solvent and Ze is the charge on the ion. The van der Waals attraction is expressed as

$$\phi_{vdW}(\underset{\sim}{R}) = -B/R^6 \qquad (2.22)$$

and frequently repulsions are expressed as

$$\phi_R(\underset{\sim}{R}) = A/R^q \tag{2.23}$$

where typically q is 9 or 12. For the general inverse power potential of the form Q/R^q, we have

$$t_{1Q} = \underset{\sim}{r}\cdot\underset{\sim}{R}\,\frac{Q}{R^{q+2}} \tag{2.24}$$

and

$$t_{2Q} = \frac{1}{2}r^2\,\frac{qQ}{3R^{q+2}}\left[(q-1) + 2(q+2)P_2(\hat{r}\cdot\hat{R})\right] \tag{2.25}$$

The electrostatic ionic-dipolar interactions are more complicated to handle. This is the case because it is necessary to consider both the location of a source dipole (a solvent molecule) as well as its orientation. In order to handle adequately the terms which are of second order in the displacement of the ion from the origin of the coordinates, we make use of the Carlson-Rushbrooke expansion.[12,13] The first order term, $t_{1CR} = \underset{\sim}{r}\cdot\underset{\sim}{F}_{CR}$, has the following components of the force:

$$f_{xCR} = a_x(2X^2-Y^2-Z^2) + 3a_yXY + 3a_zXZ \tag{2.26a}$$

$$f_{yCR} = 3a_xXY - a_y(2X^2-Y^2-Z^2) + 3a_zYZ \tag{2.26b}$$

$$f_{zCR} = 3Z(a_xX + a_yY) + a_z(3Z^2-1) \tag{2.26c}$$

with

$$F_{iCR} = -\frac{Ze\mu}{R^5} f_{iCR} \qquad (i=x,y,z) \tag{2.27}$$

and a_i (i=x,y,z) are direction cosines associated with the orientation of the dipole.

The second order term is

$$t_{2CR}(\underset{\sim}{R}+\underset{\sim}{r}) = \tfrac{1}{2}(3Ze\mu/2R^7)\underset{\sim}{r}\underset{\sim}{r}:\underset{\sim}{A} \tag{2.28}$$

with

$$A_{xx} = \tfrac{1}{2}\{a_x X[5(X^2-3Y^2-3Z^2)+3]-a_y Y[5(Y^2-3X^2+Z^2)-1]+a_z Z(20XY - 10Z^2+6)\} \tag{2.29a}$$

$$A_{yy} = \tfrac{1}{2}\{a_x X[5(X^2-3Y^2+Z^2)-1]-a_y Y[5(Y^2-3X^2-3Z^2)+3]+a_z Z(20XY - 10Z^2+6\} \tag{2.29b}$$

$$A_{zz} = 2\{(a_x X+a_y Y)(5Z^2-1)+a_z Z(5Z^2-3)\} \tag{2.29c}$$

$$A_{xy} = A_{yx} = \tfrac{1}{2}\{a_x Y[5(3X^2-Y^2-Z^2)+1]+a_y X[5(3Y^2-X^2-Z^2)+1] +20a_z XYZ\} \tag{2.29d}$$

$$A_{xz} = A_{zx} = \{a_x Z[5(X^2-Y^2-Z^2)+3]+10a_y XYZ+2a_z(5Z^2-1)\} \tag{2.29e}$$

$$A_{yz} = A_{zy} = \{10a_x XYZ +a_y Z[5(Y^2-X^2-Z^2)+3]+2a_z Y(5Z^2-1)\} \tag{2.29f}$$

With the use of eq (2.27) it is possible to show easily that the position of equilibrium for a crystalline cage of solvent dipoles, all aligned to give the optimal attraction, is also the centre of symmetry. Furthermore, with respect to that position of equilibrium, the second order term can be shown to vanish. Therefore, as we originally reported,[1] for cages of solvent dipoles

which are arranged about the centrally located ion according to the symmetries of the tetrahedron and octahedron, there is no contribution to the harmonic force constant from electrostatic terms. Any deviation from crystalline symmetry, however, does involve electrostatic contributions to the force constants. The terms listed facilitate the determination of the magnitudes of these force constants.

In our initial investigation[1] of the far infrared spectra of the solvated alkali metal cations, we employed a simple model potential energy function. Specifically, we assumed that it was possible to use a Born type of exponential repulsion, eq (2.11), together with the direct interaction between the ion and the dipole on the solvent. Other contributions to the total potential energy function, such as the interaction between the solvent dipoles in the first shell, were not included in the process of determining the values of the parameters B and ρ. Instead, we considered only the single solvent-ion contribution. The condition of equilibrium for the ion-solvent pair yielded an expression for B in terms of the dipole moment of the solvent, the charge on the ion, and the equilibrium separation. We assumed further that the value of this equilibrium separation was given as the sum of the ionic crystallographic radius and the solvent radius, as determined from the molecular volume.[1] Thus, for example, for the lithium cation solvated by dimethyl sulfoxide (DMSO), we found[1] $B = 0.23 \times 10^{-12}$ erg and $\rho = 0.19$ Å.

Subsequently, we argued[3] that if the lithium cation were electrochemically reduced at the outer Helmholtz plane to yield a solvated atom, then it might be possible to infer the values of the parameters in the Morse potential, eq (2.16), from the values of B and ρ found for the ion. In particular, we argued that because

direct electrostatic contributions do not appear in the expression for the force constant of the ion, their absence will not be missed when the atom is formed. If, on the other hand, the repulsive part of the Morse potential is essentially the same as the repulsive part--the Born term--for the ion, then it should be possible to specify the values of the dissociation energy D and the exponential quantity a as

$$B \cong D$$

$$2\rho \cong 1/a. \tag{2.30}$$

For the Morse potential, the force constant in a tetrahedral field of sources is

$$k_T = \frac{8}{3}a^2 D$$

$$\cong \frac{2D}{3\rho^2} . \tag{2.31}$$

Thus, we predicted that the atom should have a spectral maximum due to the vibration of the atom within the cage of solvent of 320 cm^{-1}.

In a subsequent paper,[2] more realistic potential energy functions were employed in order to investigate the vibrations of the alkali metal cations in cages of solvent. Potentials consisting of repulsions between the ion and solvent molecules, attractions between the ion and the dipoles on the solvent, the ionic induced-dipolar terms, and the repulsions between solvent dipoles in the first layer were considered. A variety of forms were used to model the repulsions and some of the attractions. A simple form, which gave reasonably consistent results with our general findings, consisted of the Born repulsion, an ionic induced-dipolar attraction of the form of eq (2.21), the direct ionic-dipolar attraction, and

the repulsions between dipoles in the first layer. The adjustable parameters were B and ρ in eq (2.11). The values of B and ρ were determined with the use of the expression for the force constant and the condition for equilibrium in the solvated system. We found that $B = 0.51 \times 10^{-12}$ erg and $\rho = 0.26$ Å in this calculation.[2]

With the use of these new values for B and ρ, we estimated[3] a new value of the maximum for the absorption of solvated, atomic lithium. We found in this case that the maximum shifts upward to 353 cm^{-1}. Implicit in this determination is the assumption that the parameters in the Morse potential for the atom can be identified by comparison to the repulsive Born potential.

On the other hand, if we assume that formation of the atom in its solvated state retains the values of the Born potential together with this potential form, and if further we use the a van der Waals attraction for the remainder of the potential, then we estimate a much lower value for the absorption maximum. The value we estimate for lithium in DMSO depends on estimates of the polarizability of the lithium atom using the Slater coefficients (cf. ref. 13, pp. 951-55), and a guess of the ionization potential of DMSO. Altogether, we estimate that with an equilibrium radius of solvation of 3.68 Å, the vibrational maximum should appear in the range of 100 to 150 cm^{-1}.

One can stage rather qualitative arguments to claim that the Morse potential for the atom, and the identification of parameters made above, represents a better fit. It needs to be emphasized that we have employed point dipole models to represent what most likely is a complicated molecular system. The van der Waals attraction (as estimated by London's equations[13]) is found to be quite strong.

The effect of this attractive force is to diminish the value of the force constant for the vibration of the atom in its cage of solvent. An actual potential might involve much weaker interactions which would be represented better with the use of the Morse potential. It may be possible to resolve some of these questions through the use of quantum chemical calculations. Such a programme is planned.

We conclude this section with a brief analysis of the interaction between an ion and a tetrahedral cage of solvent. We compare these results to a potential inferred for the solvated lithium atom as described above. The discussion to follow, therefore, sets the stage for the consideration of the stabilities of the solvated ionic and atomic systems in the presence of the surface of the metal.

In a previous paper,[7] we considered the question of the stability of a charge or mass located at various positions of equilibrium with respect to rings, polygons, and polyhedra. One important conclusion of that work was the demonstration of the close connection between the Taylor series for a polygon and the series which eventually is constructed for a related polyhedron. Here, we consider specifically the tetrahedron. As indicated before,[7] a tetrahedron can be constructed from a base triangle of sources together with a fourth source placed on the axis which passes through the centre of the triangle. We can use this approach to establish the conditions for equilibrium in various regions of the tetrahedron.

We rewrite the expansion for g(R) as

$$g(\underset{\sim}{R}+\underset{\sim}{r}) = \sum_{n=0}^{\infty} (r^n/n!) \sum_{\ell} A_{n\ell} P_{\ell}(\hat{r}\cdot\hat{R}) J_{n\ell}(R) \qquad (2.32)$$

with

$$J_{n\ell}(R) = \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!} R^{-q}\left(\frac{n-q}{R} + \frac{d}{dR}\right)\left(\frac{d}{dR}\right)^{n-q-1} f(R). \tag{2.33}$$

For the basic polygon, we can write[7]

$$g(\underset{\sim}{R}+\underset{\sim}{r}) = \sum_{n=0}^{\infty} (r^n/n!)\sum_{\ell} A_{n\ell} P_\ell(\cos\theta_R) P_\ell(\cos\theta_r)[NJ_{n\ell}(R)] \tag{2.34}$$

in which N is the number of equally placed sources which make up the polygon. For example, N is 3 for a triangular distribution of identical molecules.

The position of equilibrium for a system is determined with the use of the first order term:

$$\sum_{N} P_1(\cos\theta_{R(N)})[NJ_{11}(R_{(N)})] = 0 \tag{2.35}$$

where the summation over N is over sources. For a tetrahedron, three identical sources are placed on the base triangle, and an additional source is located on the axis, as indicated. For an arbitrary displacement $rP_1(\cos\theta_r)$ with respect to <u>all</u> of the sources, we can write

$$[3P_1(\cos\theta_R) + 1]J_{11}(R) = 0. \tag{2.36}$$

If $J_{11}(R) \neq 0$, then $3\cos\theta_R + 1 = 0$, or $\theta_R = 109.47°$, the tetrahedral angle. This exercise merely proves what is well known.

Suppose, on the other hand, that not all the $J_{11}(R)$ are the same. Then, the condition for equilibrium is satisfied by the more

complicated equation

$$3\cos\theta_{R_1} J_{11}(R_1) + J_{11}(R_2) = 0. \tag{2.37}$$

In order to solve this equation, it is necessary to know the functional form of the $J_{11}(R)$ terms. The equation can be simplified by noting that

$$\cos\theta_{R_1} = -\frac{1}{3}\frac{R_0+3D}{[R_0^2+D^2-2R_0D/3]^{1/2}} \tag{2.38}$$

in which R_0 is the distance of a source in the triangle from the axis which passes through the centre of the triangle. The quantity D is the displacement along the axis from an origin of the coordinate system somewhere along the axis. Clearly, when D=0, the origin is at the centre of the tetrahedron. The value of R_1 is

$$R_1 = \sqrt{R_0^2+D^2-2R_0D/3} \tag{2.39}$$

and for R

$$R_2 = R_0 + D. \tag{2.40}$$

Thus, eq (2.37) can be solved for the position of equilibrium in terms of the single parameter D.

It is not difficult to see that for some potential energy functions, there can be a second position of equilibrium with respect to a tetrahedron of sources which lies outside the volume. Indeed, for the tetrahedron, there are four equivalent positions

of equilibrium outside of the cage. These positions of equilibrium outside of the cage will be important in our considerations of the processes of desolvation of ions and atoms in the next section.

The results of several straightforward investigations of the potential energy of an ion and atom interacting with a tetrahedral cage of solvent are shown in the figures. Fig. 1 illustrates two types of interaction. For both cases only the ionic-dipolar attraction and a Born type of repulsion were considered. For the first model, Fig. 1a, the dipoles on the solvent were held rigidly in place in orientations which gave the maximum attraction at the centre of symmetry. Thus, as the ion passed from its initial position of equilibrium on out through the centre of a face of the tetrahedron, it passed from a region of attraction to a region of repulsion. This transition is clearly illustrated in the plot of the force as the ion moves. The curve for the force shows one zero for the internal minimum, and a second zero for the maximum near the place of sources which define the face of the tetrahedron. A third zero does not appear. There is no position of equilibrium for the location of the ion outside of the cage. The sum of the repulsions is too great. Thus, no stable complex can form between the externally located ion and the cage.

On the other hand, the curves for the second case were derived by allowing the dipoles to "follow" the ion out of the cage. The results are shown in Fig. 1b. In this case, clearly there is a position of unstable equilibrium near to the face of the tetrahedron. Finally, there is a second position of stable equilibrium outside of the cage. Thus, it is possible for the ion to occupy this position and to make transitions from inside to outside of the cage and back.

The second figure, Fig. 2, is similar to the first except for the addition of an ionic-induced dipolar attraction which depends upon the charge on the ion and the polarizability of the solvent. Here, as well, we consider two cases: one in which the dipoles are held rigidly in place, Fig. 2a, and the other in which the dipoles are free to "follow" the ion as it moves, Fig. 2b. In the first case, the ion moves from a position of equilibrium at the centre of the cage on out through a face. The force shows one zero at the central minimum in the potential. A second zero appears at the maximum near to the face of the tetrahedron. Again, no true second minimum appears. The strength of the Born repulsion together with the repulsive orientations of the dipoles toward the ion when the ion lies outside of the cage is too great. However, because of the strength of the ionic induced-dipolar attraction, the repulsion is not as great for the ion when it lies outside of the cage as it was for the first case, illustrated in Fig. 1.

When the dipoles are allowed to "follow" the ion, we find in this case that the combination of an attractive ionic dipolar direct interaction together with the ionic induced-dipolar attraction is sufficiently greater in magnitude compared to the repulsion that again no true minimum is found for the ion when it is found outside of the cage. However, in contrast to the first result, shown in Fig. 2a, in this case in Fig. 2b we see that the force is attractive overall. This means simply that if an ion comes under the influence of the strongly attractive cage of solvent dipoles, it will migrate to a position of equilibrium within the cage. This strength of interaction can be of importance for the consideration of the question

of ionic desolvation at an electrode interface.

The case of the solvated atom, shown in Fig. 3, illustrates a behavior which is very much like that of the case of the ion in Fig. 1b. Here, as well, we see that it is possible for the atom to occupy a position of stable equilibrium outside and inside of the cage. In contrast to the cases for the solvated ion, however, it is obvious here that the solvated atom is held much less strongly. It is interesting to note that although the strength of the binding of the atom to the cage of solvent is much weaker than it is for the ionic cases, the radii of curvature for the minima of the potential are sufficiently small to explain why the low-lying solvated atomic vibrations should be of the same order of magnitude as those for the solvated ion. It is clear that the strength of the binding of the atom to the cage falls off rapidly as the atom is displaced from its position of equilibrium at the centre of the cage.

3. The Effect of a Surface on the Stability Against Displacement

The analysis of the vibrations of ions and atoms in cages of solvent gives us some feeling for the nature of the forces which operate within these systems. We can now examine the stability of the solvated ion or atom with reference to displacements from the shell of solvent towards the surface of an electrode. In the following discussion, the lithium cation and atom are considered as example systems. These systems may offer possibilities for experimental verification.

a. Models: The models of the solvated lithium ion or atom in the electrical interface, the double layer, are the following.

For both cases a coordination number of four and a tetrahedral geometry are assumed. It is possible to consider deviations from this regular geometry. Some consideration of this has been given elsewhere, cf., ref. [14]. The primary effect of the distortion of the shell of solvent is to lift the three-fold degeneracy of the vibrations of the ion within the shell. For small deviations, however, the lifting of the degeneracy, the splitting of the vibrational levels, is not great. Arguments concerning stability in these distorted systems parallel the arguments used for the more regular, crystalline cases of solvation. The results are essentially the same. We consider the crystalline cases as they are easier to visualize geometrically, and they are easier to treat mathematically in this first instance.

For the ion, the cage of solvent is considered to consist of point dipoles embedded within the molecular mass. The solvent molecules themselves are considered to be spherical, as an approximation. The effect of finite size is introduced with the use of an exponential repulsion of the Born type. The accuracy of this spherical approximation is doubtful when applied to extended, polyatomic molecules. Thus, the actual heights of barriers to desolvation, etc., will not be estimated accurately with this model. Nevertheless, we believe that for the purposes of this preliminary type of analysis, some general trends toward desolvation ought to emerge. The approximation is easily amended to include additional interactions between the migrating ion and specific atomic and electronic "parts" of the various molecules of solvent the ion encounters.

For the two cases, ionic and atomic, the cage of solvent is

aligned so that one of the tetrahedral faces is coplanar with the surface of the metallic electrode. The ion or atom is then allowed to move along a vector which passes through the centre of the face and on to the surface of the metal. The potential energy for the ionic or atomic system is evaluated for points along the length of this vector. In addition, radii of curvature of the potential energy functions are found for the same points. At a minimum or maximum in the energy, the radius of curvature is the same as the force constant. The sign of this quantity determines the stability of the system against further displacement along the path to the surface.

The interactions between the solvated systems and the surface of the metallic electrode are the following. For the case of the ion, we assume that the ion interacts with the metal through image forces and through a partial covalent force which is represented in terms of the Morse potential. It is of course difficult to obtain information about the binding energy of a lithium ion on to the surface of a wet electrode. We estimate it to be about one third of the bond energy of the Li_2 molecule. An attraction of this magnitude seems to be reasonable.

For the case of the solvated atom, on the other hand, we assume that the atom interacts with its surrounding solvent and with the surface of the electrode through appropriate forces which have their origin in the Morse potential. The bond energy of the lithium atom on the surface is assumed to be of the order of 1.14 eV. The Morse exponent a is assumed to be $1.2 \times 10^{8} cm^{-1}$. The values of the dissociation energy D and a which are needed for the interaction between the solvent and the lithium atom are those

previously found: D = 0.144 eV and a = 2.63 x $10^8 cm^{-1}$.[3]

Finally, both for the ion and for the atom, we assume that a translation through the face of the tetrahedron of solvent which is nearest to the surface of the metal is the optimal route for the process of desolvation. The solvent can be located at the following places: $(0,0,R_0)$, $(,2\sqrt{2}R_0,-R_0/3)$, $(\sqrt{2/3}R_0,-\sqrt{2}R_0/3,-R_0/3)$, and $(-\sqrt{2/3}R_0,-\sqrt{2}R_0/3,-R_0/3)$. In a system in which the solvent is arranged in this manner, a displacement in the direction of the surface takes place along the vector (0,0,-r). Thus, in order to evaluate the forces and force constants we need only consider the Z-components given in the last section for the various contributions to the potential energy functions.

b. Stability in the tetrahedron of solvent: In the following discussion it proves to be simpler and more illustrative to work with the Morse potential alone. The figures summarize similar results for the ionic systems.

To begin, we return to the consideration of the equilateral triangle of sources, molecules of solvent, aligned to be coplanar with the surface of a metal electrode. Initially, we ignore the presence of the metal.

It is clear that the origin and centre of symmetry (X=Y=Z=0) is a valid point of equilibrium for the system. It is the centre of the triangle of sources. For reference, the sources for this system can be located at the positions: $(\pm\sqrt{3}R/2,-R/2,0)$ and (0,R,0). In each of these cases, $P_2(0) = -1/2$. Thus, the force constant for an axial displacement of the test atom in the system is

$$k_M = \frac{6aD}{R} \exp[a(R_0-R)]\left(1 - \exp[a(R_0-R)]\right). \qquad (3.1)$$

If $R < R_0$, then the axial motion at the centre of the triangle of sources is unstable. This condition has been shown before to apply both to the continuous ring and polygon of source.[7] The condition for stability, therefore, requires that the source molecules lie at distances away from the centre of the system which are equal to or greater than the equilibrium distance R_0, a characteristic of the Morse potential. The instability which arises when the test atom is placed in the centre of the triangle traces simply to the fact that all the interactions between the test atom and the surrounding molecules lie in the short-ranged, repulsive region of action of the Morse potential. Were the triangle larger, an atom could be accomodated at the centre, in a condition of stable equilibrium, as each pair-wise interaction about the point of equilibrium for the system would lie in the attractive region of the Morse potential.

A tetrahedron is formed by placing a fourth source molecule on the Z-axis. The molecules originally in a plane with reference to the point of equilibrium must be displaced a distance -R/3 along the Z-axis. The new source is located at the position (0,0,R). The force constant for this tetrahedral system now breaks down into two distinct parts: one part for the plane of source molecules which form a triangle, and the other part for the new source which lies on the Z-axis at (0,0,R). The contribution to the total force constant at the centre of solvation which is due to the three molecules located at the positions $(0,2\sqrt{2}R/3,-R/3)$, $(\pm\sqrt{2/3}R,-\sqrt{2}R/3,-R/3)$ is

$$k_{M(a)} = \frac{2}{3} a^2 D \exp[a(R_0-R)]\Big(2 \exp[a(R_0-R)](1-4/aR) - 1 + 8/aR\Big). \quad (3.2)$$

The single contribution from the source at (0,0,R) is

$$k_{M(b)} = \frac{2}{3} a^2 D \exp[a(R_0-R)]\Big(6 \exp[a(R_0-R)] - 3\Big). \quad (3.3)$$

The net result can be expressed as

$$k_M = k_{M(a)} + k_{M(b)}$$

$$= \frac{8}{3} a^2 D \exp[a(R_0-R)]\Big(2 \exp[a(R_0-R)](1-1/aR) - 1 + 2/aR\Big). \quad (3.4)$$

If $R = R_0$, eq (3.4) reduces easily to

$$k_{M(0)} = 8a^2 D/3, \quad (3.5)$$

the result previously found.[1]

c. The effect of the surface: We now consider the placing of a fifth source in the system. This source is located at the position (0,0,-R'). Such a source could represent another solvent molecule. However, more importantly for our considerations, it can represent the effective interaction of the atom at the centre of solvation with the surface. In order to express the force constant for this system,

the force constants (3.2) and (3.3) are combined with another term of the form (3.3) which represents the surface. Thus,

$$k_{M(agg)} = \frac{2}{3} a^2 D \exp[a(R_0-R)]\left[2 \exp[a(R_0-R)](1-4/aR) - 1 + 8/aR\right] + \frac{2}{3} a^2 D \exp[a(R_0'-R')]\left[6 \exp[a(R_0'-R')] - 3\right] + \frac{2}{3} a''^2 D'' \exp[a''(R_0''-R'')]\left[6 \exp[a''(R_0''-R'')] - 3\right] \quad (3.6)$$

in which R is the radius of the three (equidistant) sources which are distributed about the Z-axis, R' is the distance the point of equilibrium has shifted along the Z-axis, and R" is the distance from the point of equilibrium to the surface.

The important question to ask at this point is whether there can be instability at the point of zero force. If the system is intrinsically unstable, then once the solvated atom is formed, it should either desolvate automatically or proceed to a more stable form of solvation. It is possible, in fact, to see the emergence of stable, solvated surface species. Such species may not correspond to bound surface atoms (or ions).

We know, from the discussion immediately above, that the simple triangle of sources yields a stable central position of equilibrium if $R > R_0$. Suppose that $a'' = a$ and $D'' = D$. And, further, suppose that for the triangle of sources $R = R_0$. Then eqn (3.6) reduces to

$$k_{M(agg)} = \frac{2}{3} a^2 D + \frac{4}{3} a^2 D \exp[a(R_0-R)]\left[6 \exp[a(R_0-R)] - 3\right]. \quad (3.7)$$

This system is <u>unstable</u> whenever $a(R - R) > \ell n 2$. However, it is more

important to note the fact that when both axial sources are of equal strength, the point of equilibrium lies in the middle of the triangle of sources. If the system is stable toward an axial displacement, then the point of equilibrium corresponds to a true minimum in the potential energy. Therefore, it is possible for the atom to occupy a position at the centre of a five-fold symmetric cage of solvation. This, if course, is a conclusion which does not require elaborate mathematical justification.

On the other hand, if the fifth source on the Z-axis is not another identical molecule of solvent, it is still possible that the strength of that source will satisfy similar conditions. The atom, therefore, may be able to occupy a cage of solvent in a displaced position, a position which is displaced with respect to the centre of solvation of the atom in the free solvated state. The effective cage consists of the solvent and the surface of the metal electrode. However, it is a state for which true bond formation to the surface cannot be justifiably defined. As we discuss more in detail in the next section, in the presence of the metal it is possible for the combination of the solvent and the surface to result in the formation of a double potential well with only a small barrier between the wells. Thus, essentially, the combination of solvent and metal yields a broad, flat-bottomed potential energy well.

Although we have concentrated our attention on the formal analyses for stability in solvated atomic systems, similar analyses are formulated for the solvated ionic systems. Figures 4 through 9 illustrate the potential and the force for ions and atoms under the influence of cages of solvent and the metal surface.

The analyses for stability in the solvated ionic systems are understandably complicated by comparison to those carried out here with reference to the Morse potential. For the ionic system more terms are involved. Hence, computer assistance is required.

Also, in the preceeding discussion, we have limited our considerations to regular, symmetric distributions of solvent. It is of considerable interest to explore the possibility that there may exist deviations from the regular distributions of solvent which would be intrinsically unstable with respect to solvation. Under such a condition of instability, one would expect the solvated species, ionic or atomic, to desolvate readily. We have carried out a number of computer-assisted analyses in attempts to find cases of intrinsic instabilities both for the solvated ionic and atomic systems. Our approach simply was to begin with the crystalline cage of solvent and to perturb the locations of the molecules and orientations of the dipoles. This was done with the use of a random number generator. The random number generator assigned, sequentially, new values to the coordinates for all species. In no instance did we discover any intrinsic instability for any moderate ($\leq$0.5Å) displacement of the location of any molecule of solvent. Solvated systems seem, by virtue of our analyses, to be remarkably stable toward the spontaneous exit of an ion or an atom from its cage of primary solvent molecules. This is not to say that diffusional migration is impossible. On the contrary, diffusion is certain. However, it is an <u>activated</u> process which requires the passage of the system over a potential energy barrier.

4. Discussion

On the basis of the results we have obtained, at this point it seems to us to be appropriate to suggest that a proper definition of an adatom should be the following. An adatom exists as the state in which a metallic atom located at or near to the surface is solvated and associated with the surface. However, the metallic atom is not bound to the surface as part of the crystalline structure of the lattice. The atom occupies a position of equilibrium at the centre of a cage of solvent and metal. The location of this position of equilibrium is shifted away from the centre of solvation toward the metal.

This definition, although not alien to the standard notion,[15] does impose stronger conditions on how the notion is applied. To be specific, the formation of an adatom requires the cooperative expansion of part of the cage of solvent so that a new position of equilibrium can be formed. This new equilibrium involves the surface of the metal. Such an expansion is easily possible for a number of states of coordination. More important, however, is the degree of "tightness" which can be associated with the coordination. If the solvated atoms are tightly encaged, obviously it is true that the cooperative fluctuation needed to expand part of the cage to the extent that a new, common, and true position of equilibrium can be formed with the surface is all that much less likely. The energetics of such a large scale deformation are obvious.

All that we have said about the state of solvation of an atom in the free state and at the surface, applies equally to the ion. The analysis of the ionic system parallels that of the atomic system.

The results are summarized in the figures.

Figures 4 and 5 illustrate the solvated ionic system for the case in which the centre of the cage of solvent is located at a distance 7 Å from the surface of the metal. Figures 7 and 8 illustrate the case in which the cage is located 4 Å from the surface. At large distances, 7 Å or more, the solvated ion is essentially undisturbed by the surface. The free state, as revealled in the far infrared spectrum, is evident. As the ion moves through its cage to a position closer to the surface of the electrode, it is possible to see the presence of various minima in the potential energy functions. The number and character of the minima depend on the model potential energy function used, viz., dipoles fixed, dipoles free to follow the ion, the presence and absence of ionic-induced dipolar interactions, etc. The first minimum is associated with the presence of the ion inside the cage of solvent. The interaction is modified by the presence of the surface of the metal. The other prominant minimum is associated with the ion at the surface of the metal. However, as we note shortly, this surface-associated minimum may not be at all real.

As the centre of solvation moves closer to the surface of the electrode, it is possible to see the disappearance of some of the middle minima. Finally, the strength of interaction is sufficiently great that only a single barrier remains.

In Figs. 7 and 8 the case for which the centre of solvation is 4 Å from the surface most closely corresponds to the adionic state. The difference in energy between the solvated and surface-associated states is not great. It is possible therefore to expect that considerable migration between these two states is possible.

The energy of activation for such migrations should be small, of the order of kT.

If we consider the cases illustrated by Figs. 4 and 5, we note that the calculation oversimplifies reality somewhat. For a 7 Å separation of the centre of solvation from the surface, it is certain that there will be additional molecules of solvent in the region between the primary cage and the surface. Thus, in fact, if the ion were to migrate from its original cage at approximately 7 Å from the surface toward the surface, it is altogether possible that the ion will occupy a new position in a cage which manifests a potential of the form illustrated by Figs. 7 and 8. Therefore, the sharp and reasonably deep minima shown in Figs. 4 and 5 for the surface-associated ion are probably not likely to be found in any real system. As a consequence, the adionic state is as we have defined it.

We temper our conclusions with the following observations. First, it is possible to consider the formation of an adionic state. Our calculations, as illustrated by Figs. 4-9, suggest that a state of close association might be thermodynamically favoured as compared to the free, solvated ion (at least as far as the reduction is concerned). It needs to be noted, however, that the incorporation of the solvated ion at the surface of the electrode requires additional work terms which have not been considered. In particular, no consideration has been given either to the work which is associated with ionic diffusion through the layers of solvent in the interface to the electrode, or to the migration of the solvated species to the surface. In many instances, solvent is specifically adsorbed at the surface of an electrode. The orientation

of this adsorbate may be such as to preclude the easy incorporation of any ion or atom in an adionic or adatomic state at the surface. Moreover, as noted previously, the simple models discussed here ignore the complicated characteristics of the polyatomic solvents. Real barriers to diffusion surely are much higher than those indicated here. For any polyatomic solvent, the ion or atom does not merely see the main dipolar species, but also it sees dipolar attractive (or repulsive) and overlap repulsive contributions from other groups on the molecules (e.g., the methyl groups of DMSO or acetonitrile). Thus, there is more than just a fleeting chance that the reduction of a cation can take place in the region of the outer Helmholtz plane. There is the possibility that significant concentrations of the adion cannot form at the surface. The existence of zero-valent transition metal complexes lends support to the possibility that metallic deposition can take place by means of the primary reduction of the cation near to the bulk of the solution.

In summary, we find that there is reason to suspect that it is possible for a metallic cation to be reduced electrochemically to the state of a solvated metal atom near to the surface of an electrode. In many instances the decomposition of the state of solvation of the atom should be energetically easier to accomplish to form the atomic deposit on the metal surface than is the case for the decomposition of the state of solvation of the ion to form a surface-incorporated ion devoid of solvent.

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Figure Captions

Figure 1a. The potential energy and force for a solvated lithium cation in a tetrahedral cage of DMSO molecules. The dipoles of the solvent are oriented towards the centre of symmetry and remain fixed in that orientation. The ion is allowed to move from the centre of symmetry along any one of the C_3 axes. A negative displacement moves the ion toward the solvent molecule which lies on the axis. A positive displacement moves the ion toward, and eventually on through and out of the tetrahedral face. These movements of the ion in the cage of solvent trace the potential energy curve illustrated in this and the following figures for the solvated ion and atom of lithium.

The interaction in this case, and in 1b, consists only of the direct ionic-dipolar terms and an exponential repulsion of the form $B \exp[-(R-R_0)/\rho]$.

Figure 1b. The dipoles of solvent are allowed to "follow" the ion as it moves through the cage of solvent. NOte, the force indicates the presence of a minimum outside of the cage of solvent.

Figure 2a. The dipoles on the solvent are held rigidly fixed, oriented optimally toward the cnetre of symmetry of the tetrahedral cage. The potential consists of an exponential repulsion, the direct ionic-dipolar interaction, and the ionic-induced dipolar interaction. The force indicates only one minimum which lies within the cage.

Figure 2b. The dipoles of solvent "follow" the ion, but, as in Fig. 1b, the centre of mass of each molecule of solvent remains at its

regular tetrahedral location. There is only one minimum. In fact, in this case, the attraction is sufficiently strong that an ion approaching the cage from the outside would accelerate along the C_3 axis and seek the minimum in the centre of the cage.

Figure 3. The solvated atom in the free state is illustrated in this figure. The pair potential is described by the Morse function. Compared to the ionic systems, the scale in the figure exaggerates the depth of the well inside and outside of the cage. Nevertheless, the radius of curvature of the potential function in the region of the minimum is similar to that of the solvated ionic system. Thus, the force constant and frequencies for the solvated atomic vibrations are expected to be similar to those of the solvated ion.

Figure 4a. In this and the following figures (5 & 6) the centre of symmetry of the solvent cage is located 7 Å from the surface of the electrode. The electrode itself is modelled only with a single atom (or a simple plane, when image interactions are considered). In this case, the dipoles of solvent are oriented towards the centre of symmetry of the cage of solvent. The potential energy function consists of electrostatic terms, , viz., ionic-dipolar interactions and image terms, and an exponential repulsion. As the ion moves through the cage of solvent, the dipoles remain fixed, pointing towards the centre of symmetry for the cage.

The plot of the force indicates several zeros, however, there only two true minima: one near the centre of the cage of solvent and the other near to the surface of the electrode. Note that the second minimum at the surface of the electrode may be spurious--see text--

as the calculations used to derive these potential functions ignore any solvent in the region between the cage and the surface.

Figure 4b. The solvent dipoles are allowed to "follow" the migration of the ion in this case. As in the case of the free, solvated ion, here as well we see a minimum outside the cage of solvent. It is a potential minimum which exists independently of the minimum at the surface of the electrode.

Figure 5a. The dipoles are held rigidly fixed, oriented toward the centre of symmetry within the cage of solvent. The potential energy consists of the ionic-dipolar direct interaction, the exponential repulsion, and the ionic-induced dipolar interaction. No intermediate minimum appears between the cage of solvent and the surface of the metal in this case.

Figure 5b. The dipoles "follow" the ion. Again, no intermediate minimum appears.

Figure 6. This figure illustrates competing forces, derived from Morse potentials, acting on the solvated atom. It is obvious that with respect to the values of the parameters used, the activation energy for the transition from the solvated atomic to the surface-associated (adsorbed, adatomic) state is small. Although there is a shallow intermediate well, its existence is probably spurious--for the same reasons that the ionic well may be spurious. In any case, the barrier to desolvation for the atom is much lower than is the case for the ion.

Figure 7a. In this case, and in the following two figures (8 and 9),

the centre of symmetry of the cage of solvent is located 4 Å from the surface of the electrode.

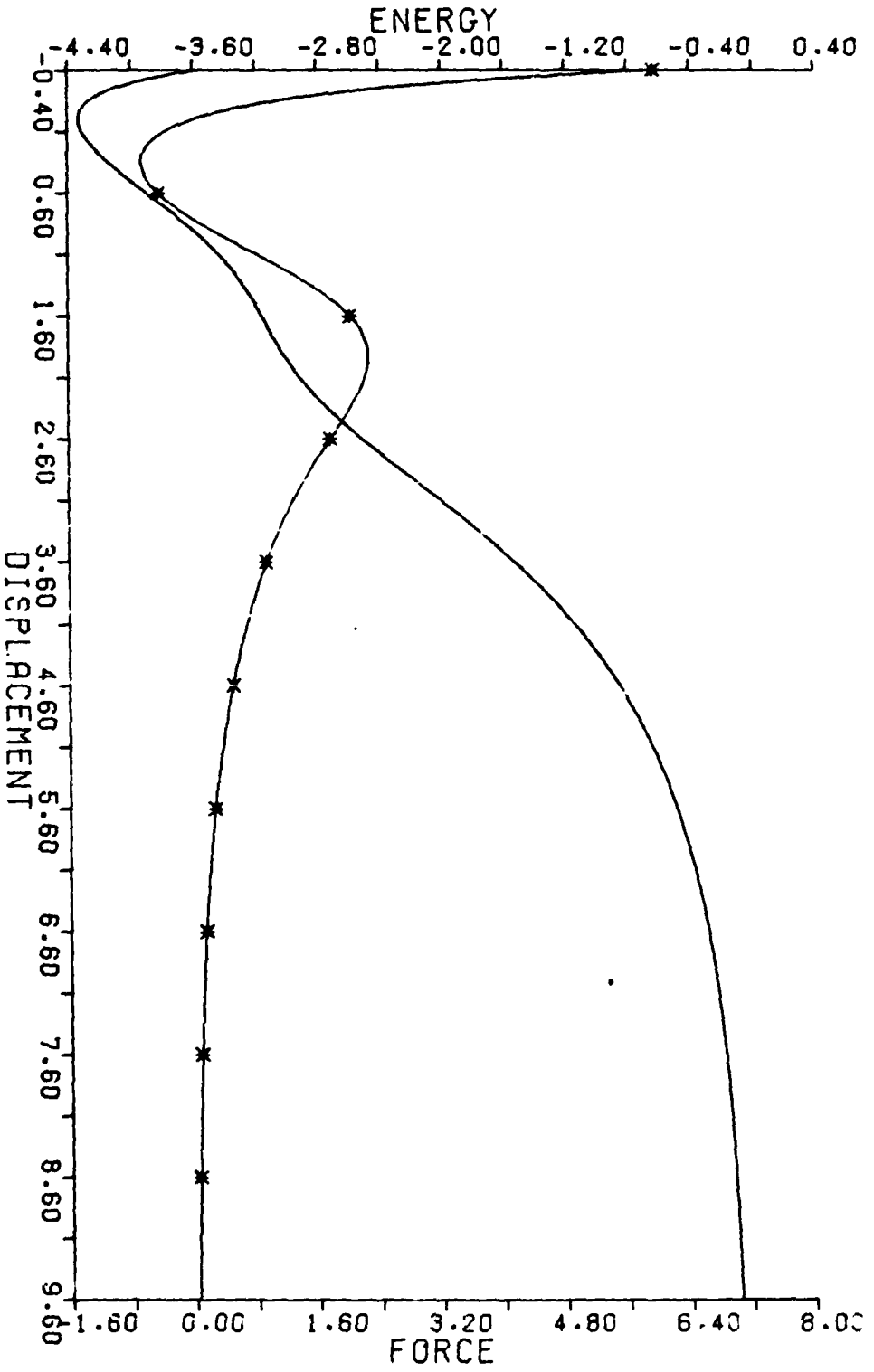
In this case the potential energy function consists only of the ionic-dipolar, direct interaction and the exponential repulsion. The dipoles are held fixed, oriented toward the centre of the cage of solvent. In this model, there is still a barrier to the migration of the ion from the cage of solvent to the surface of the electrode. Figure 7b. In this figure, the case of the freely rotating dipoles is illustrated. A barrier to desolvation remains.

Figure 8a. In this figure, the dipoles are held fixed. The potential consists of the ionic-dipolar terms, the exponential repulsion and the ionic-induced dipolar attraction. As the figure indicates, there ramins a slight barrier to desolvation. However, the surface-associated state appears energetically to be much more stable than would be the case for the solvated ion at this close a distance from the electrode surface.

Figure 8b. When the dipoles are allowed to move freely, it appears that the surface-associated state is accessible from the solvated state by means of a barrierless transition. The stability of this state over that of the solvated ion is due to the combination of ion-solvent attractions plus the attraction between the ion and the surface.

Fiugre 9. The association of an atom with its shell of solvent and with the surface is shown. There is a small barrier which exists between the solvated and surface-associated states. The well system is roughly symmetrical. Thus, during the lifetime of such

an association, the atom ought to be able to make easy transitions from states of association with the solvent to states of association with the surface, and back.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-1.20
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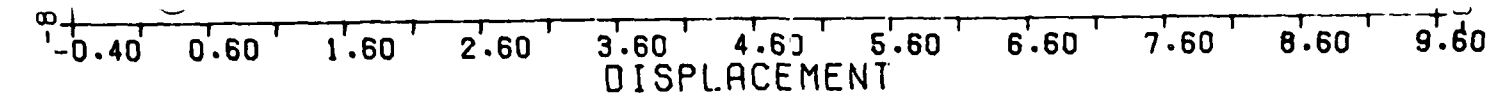
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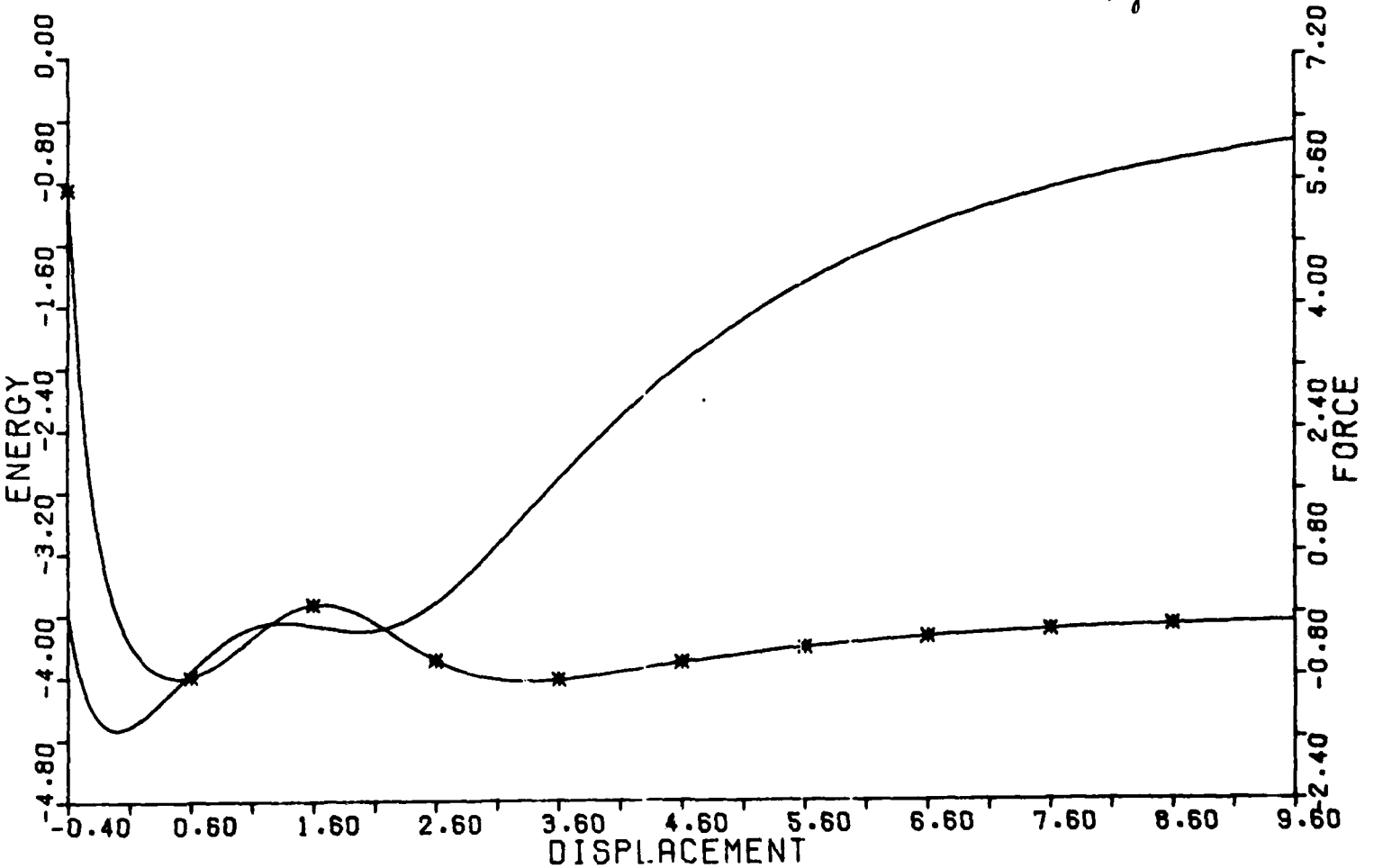
DISPLACEMENT

Fig 15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-4.00
-4.80
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2.40
0.80
-0.80
-2.40
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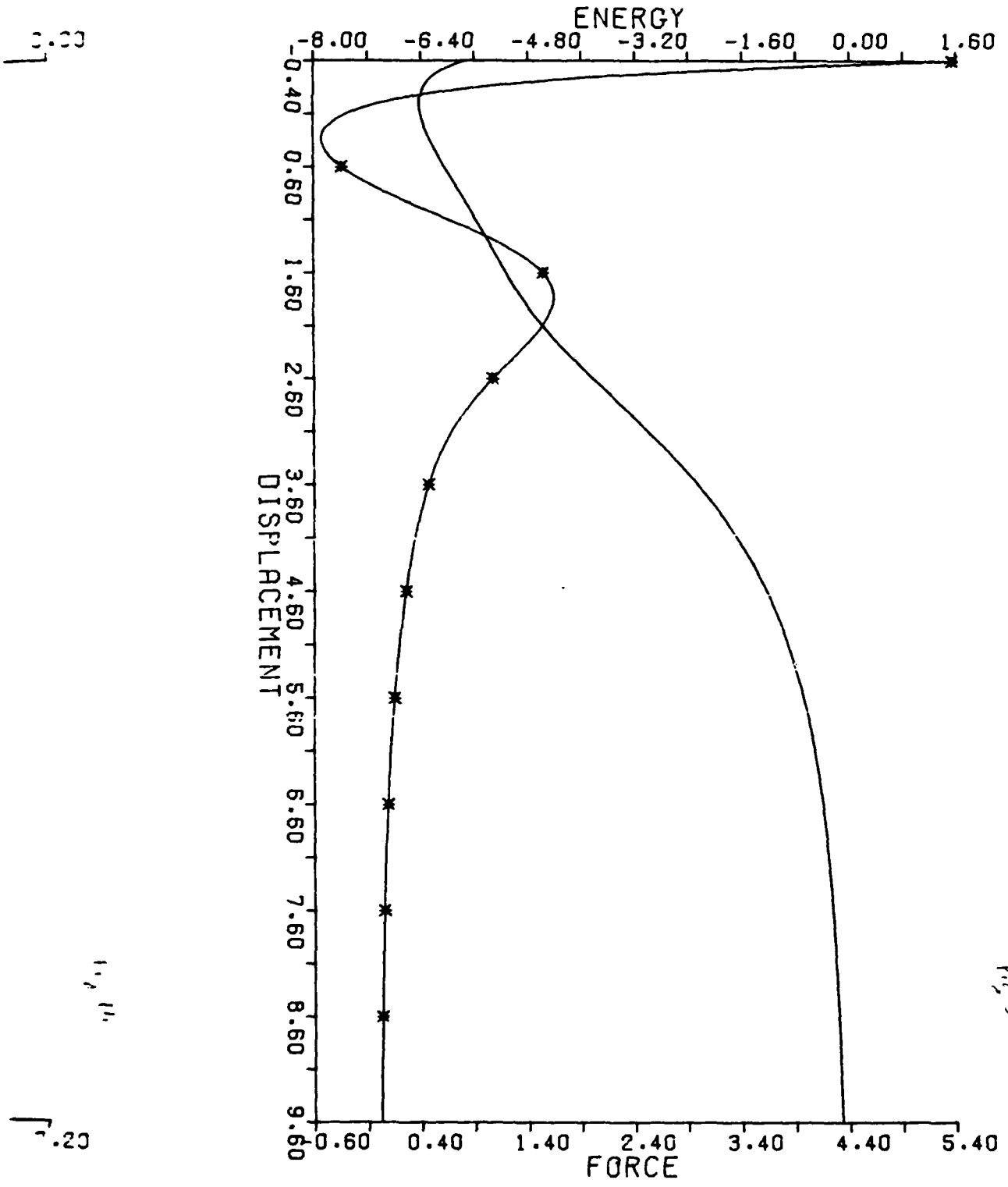
DISPLACEMENT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3.60
4.60
5.60
6.60
7.60
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DISPLACEMENT
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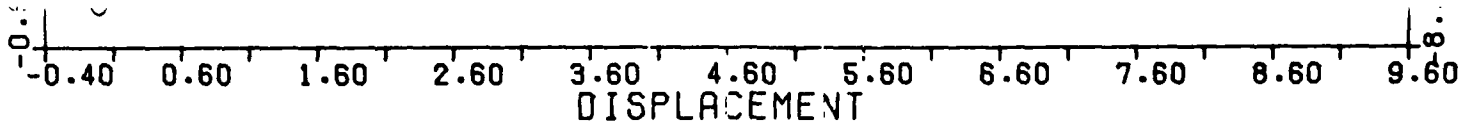
2.40
3.40
4.40
5.40
FORCE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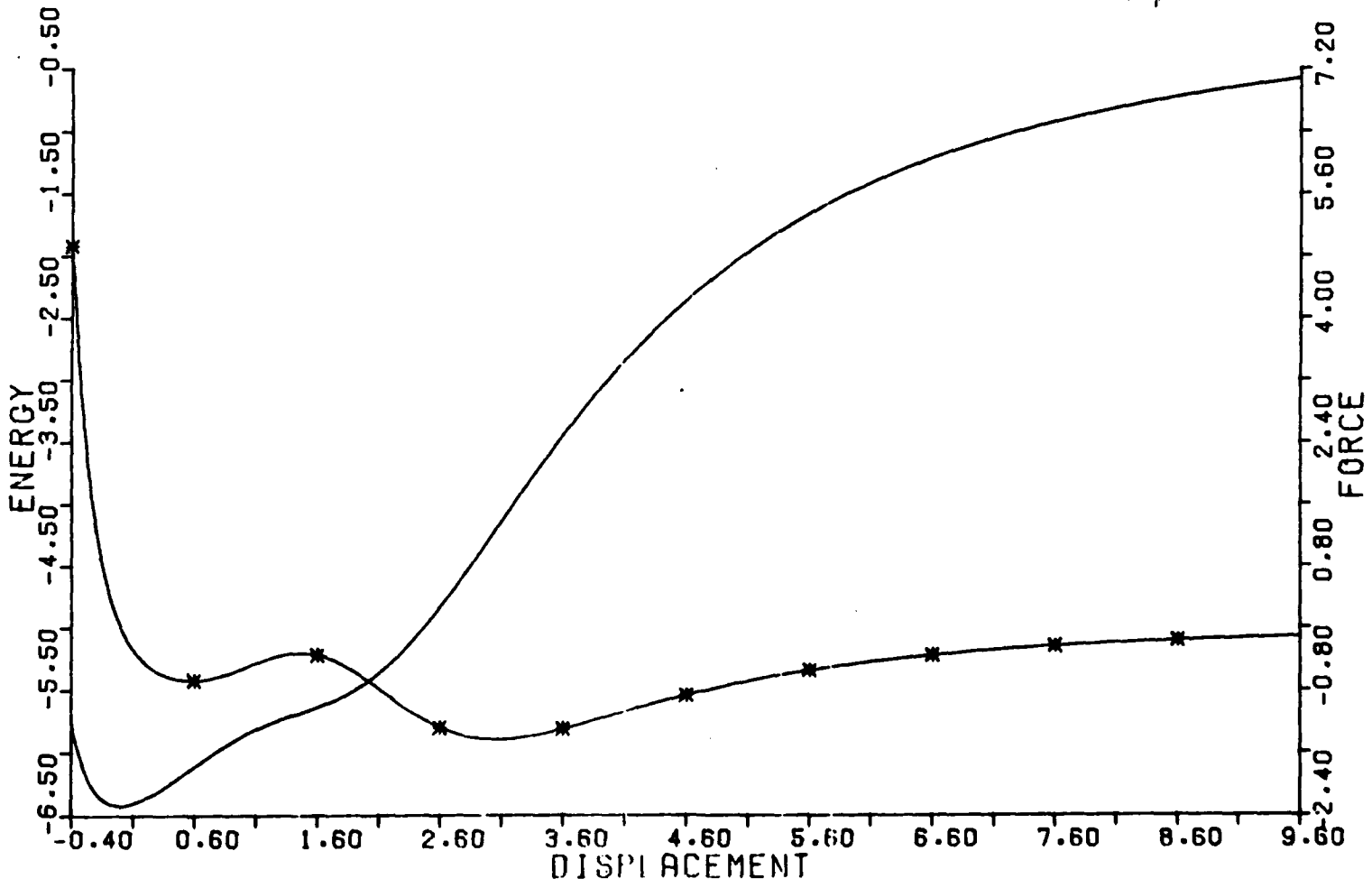
DISPLACEMENT

Fig b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-0.80
-2.40
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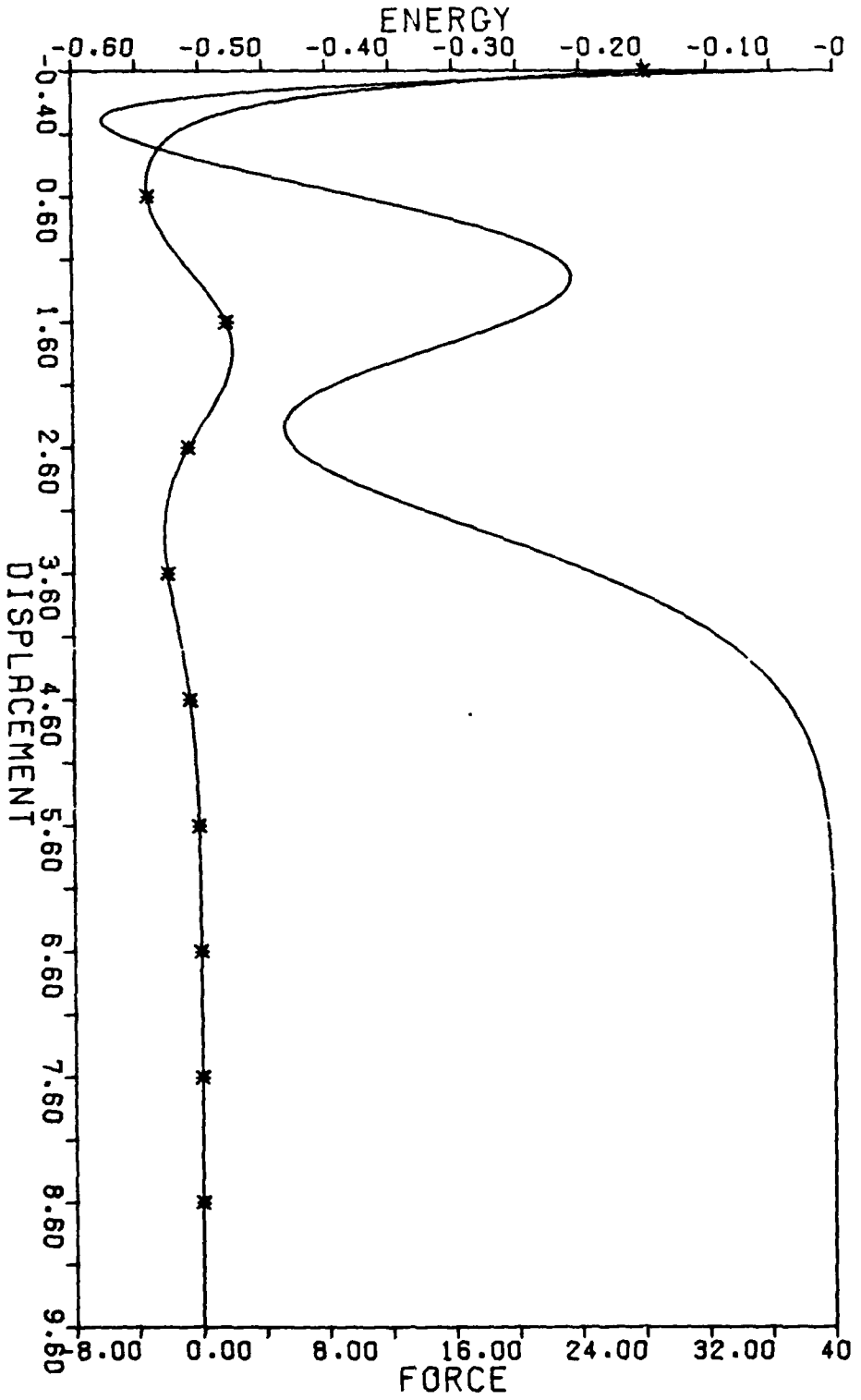
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4.60
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6.60
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DISPLACEMENT
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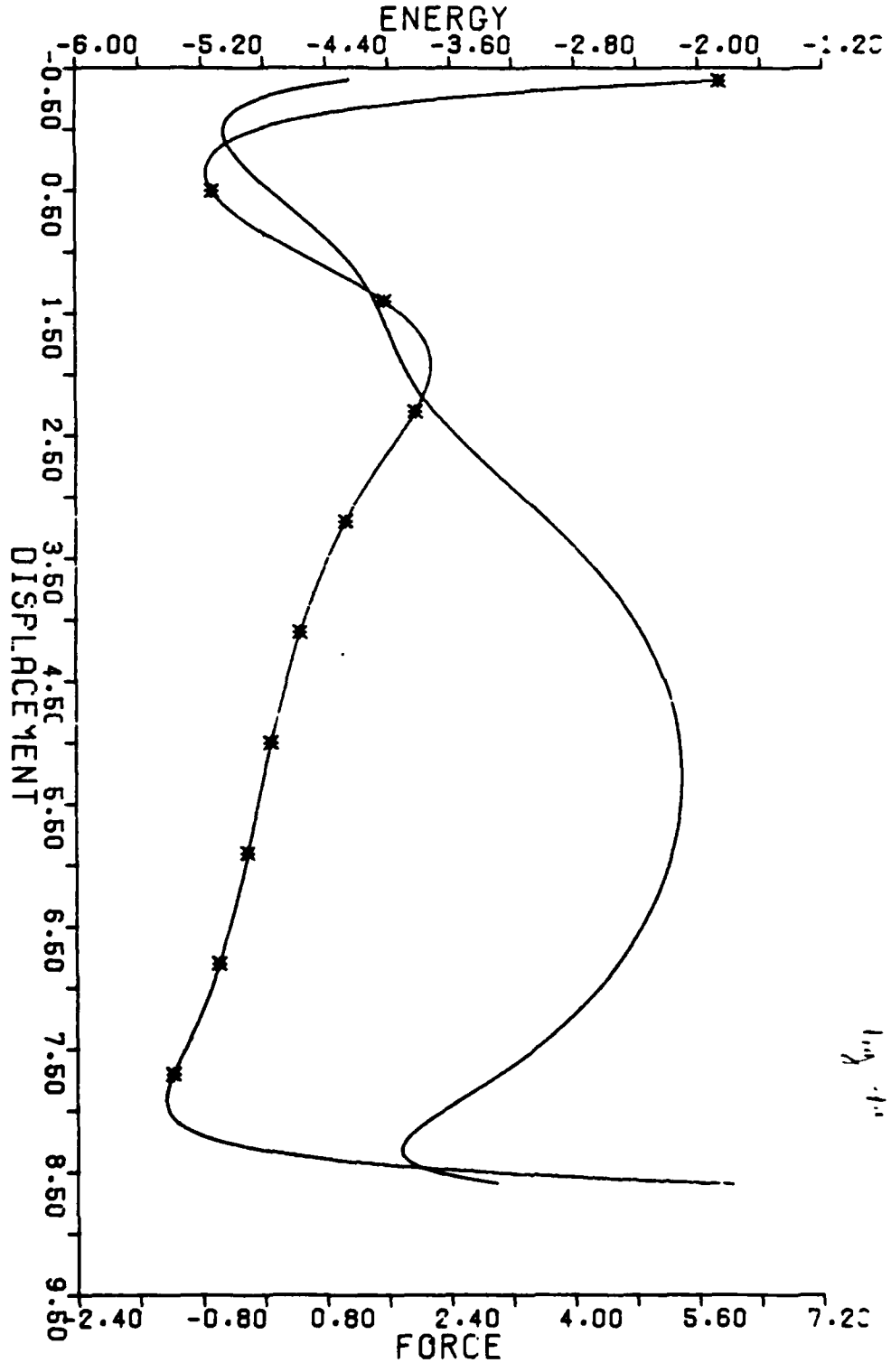
16.00
24.00
32.00
40
FORCE

Fig 3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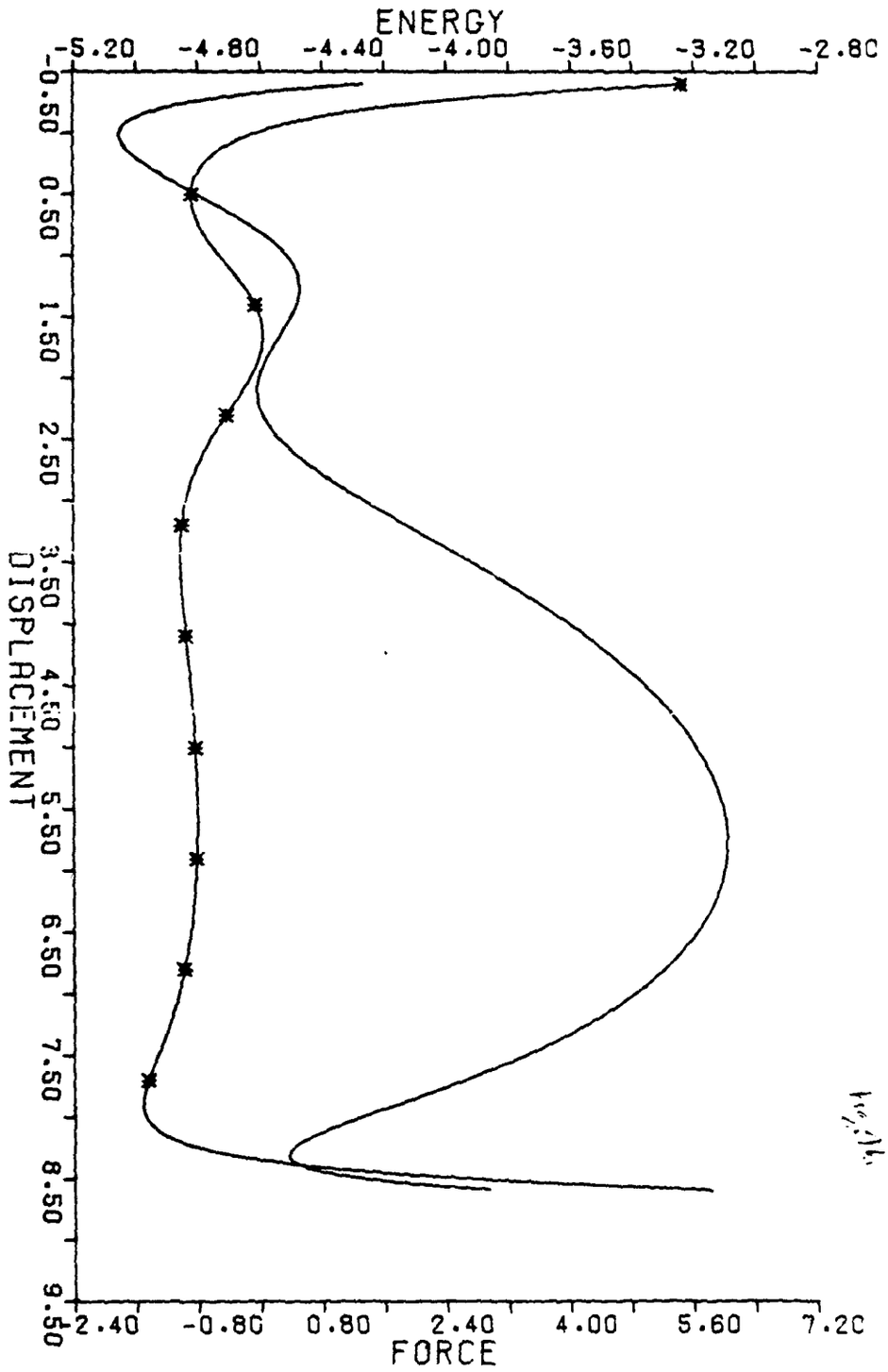
FORCE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FORCE

Fig 5a

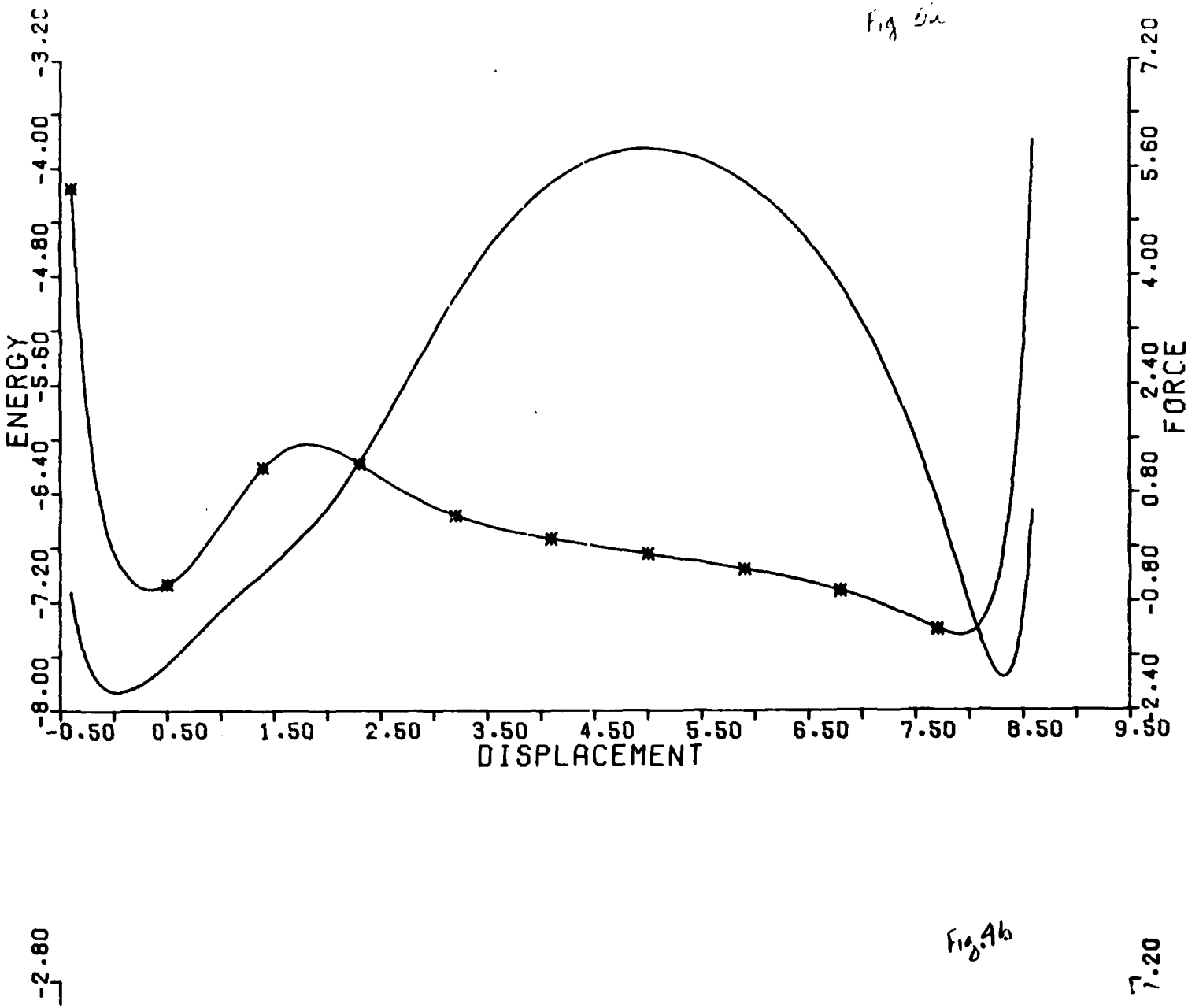

Fig. 4b

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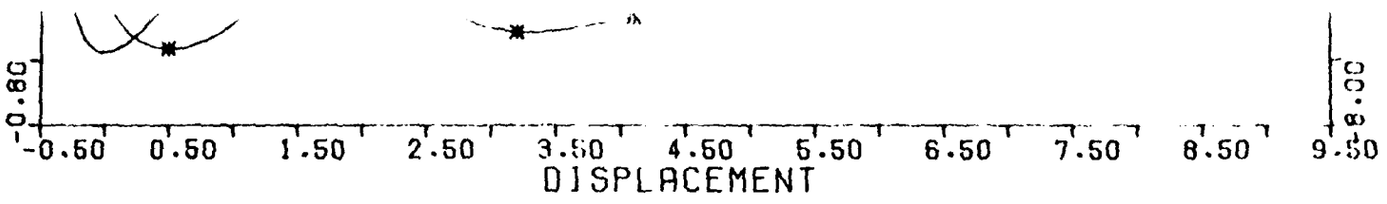
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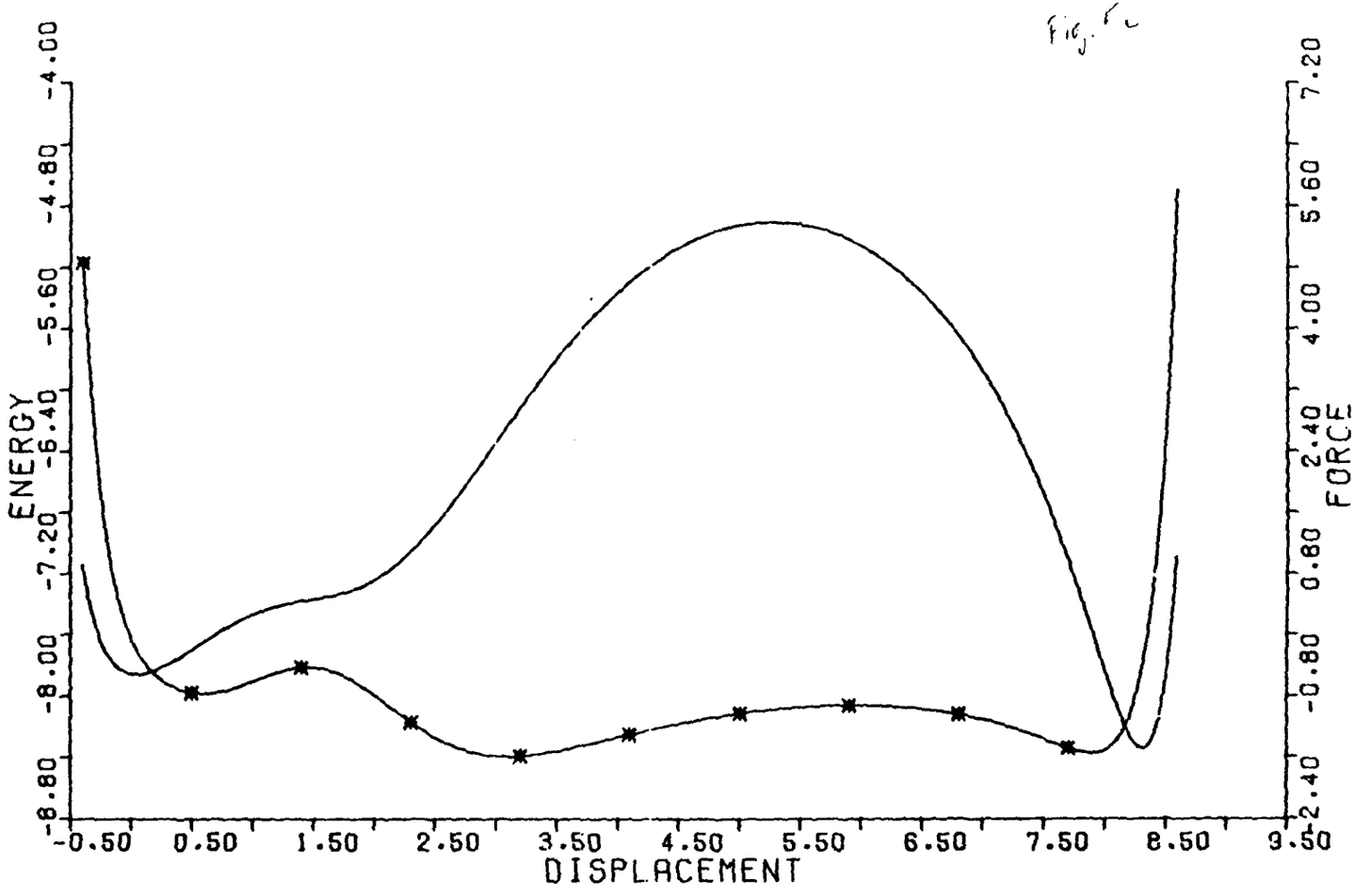
DISPLACEMENT

Fig. 5c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DISPLACEMENT

Fig. 6

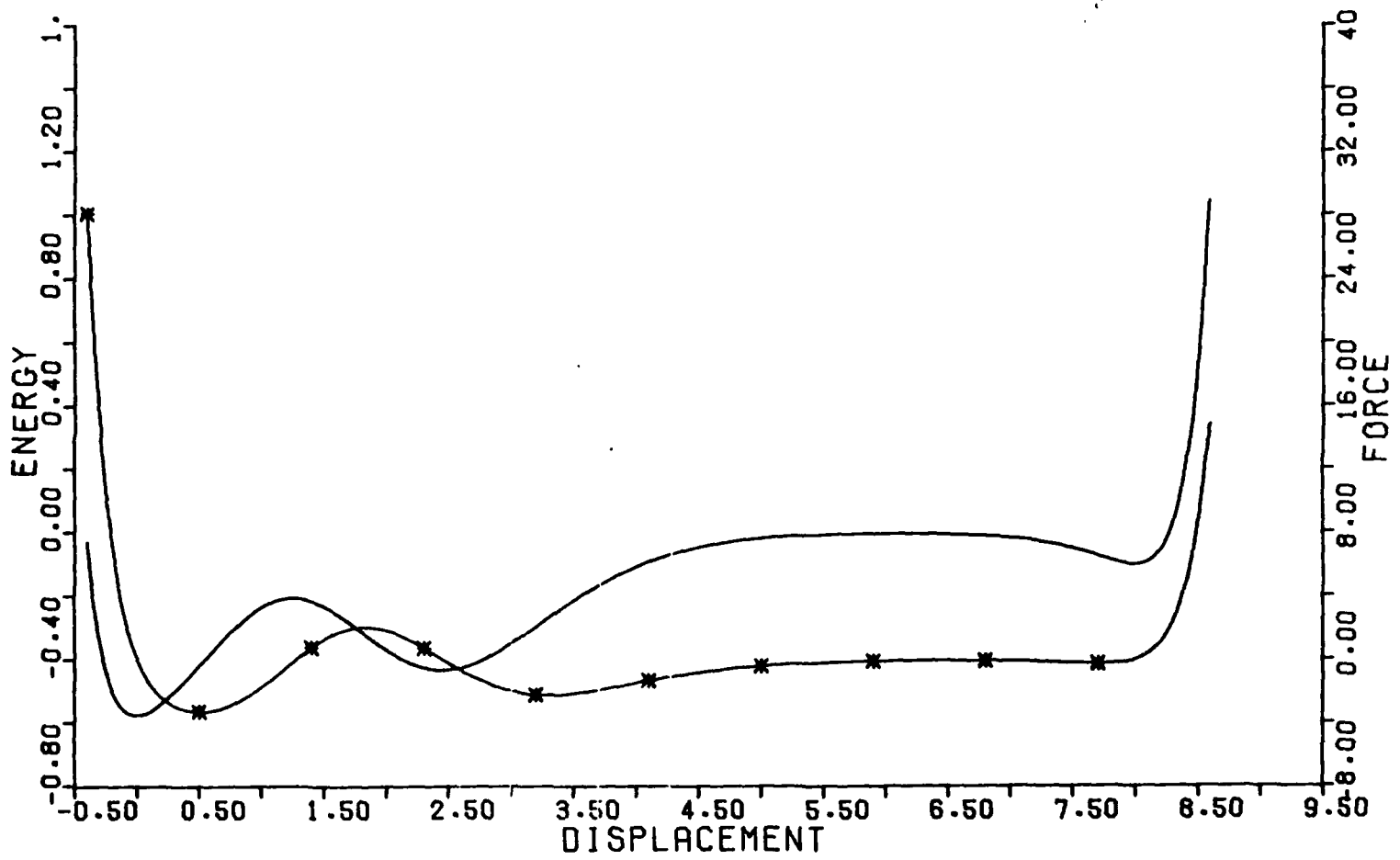

Fig. 5b

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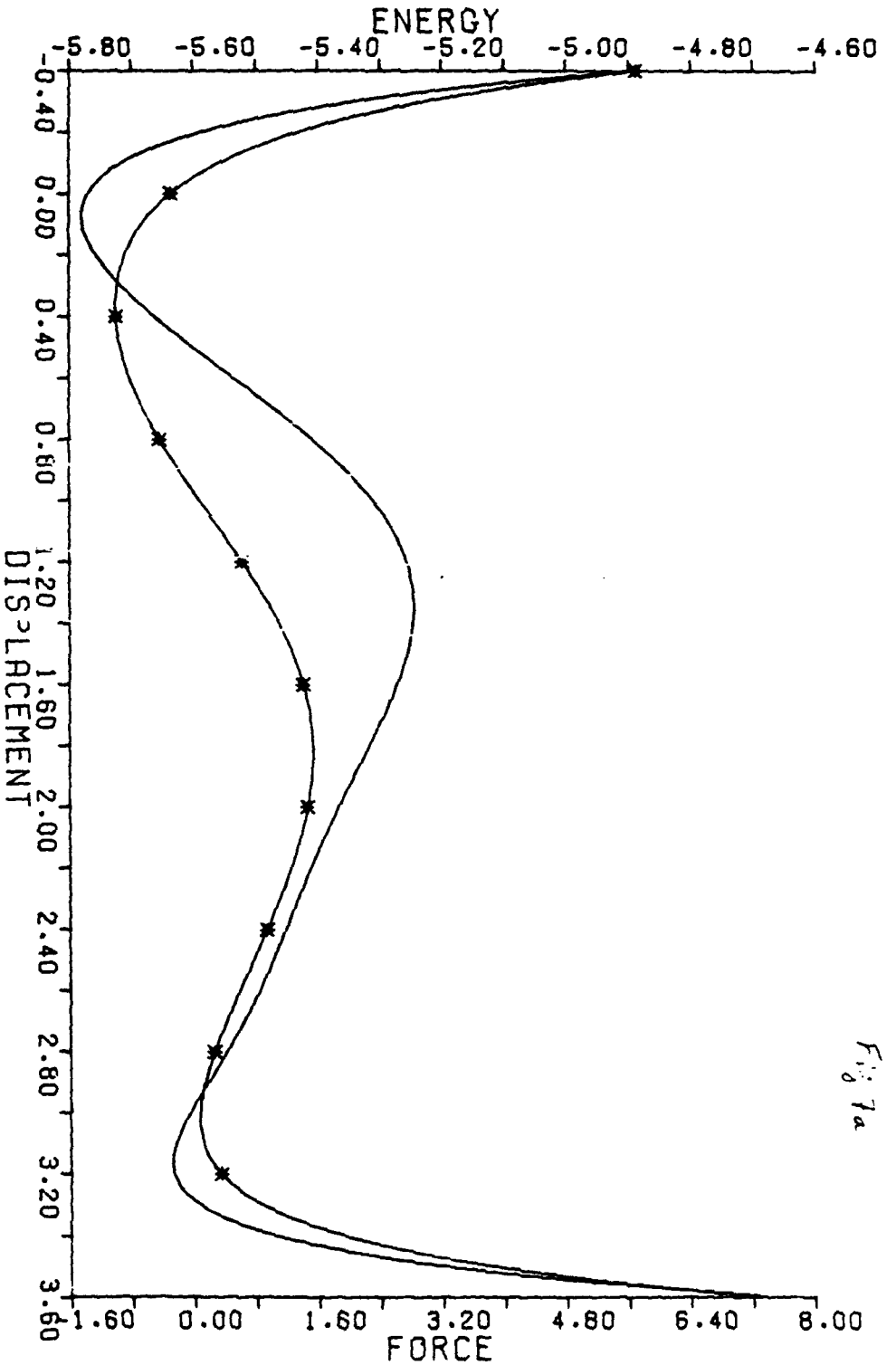
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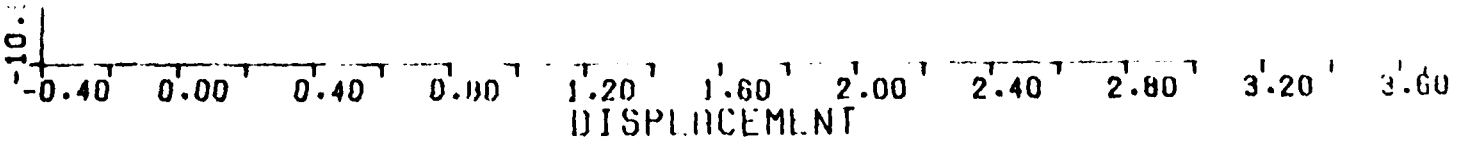
FORCE

Fig 7a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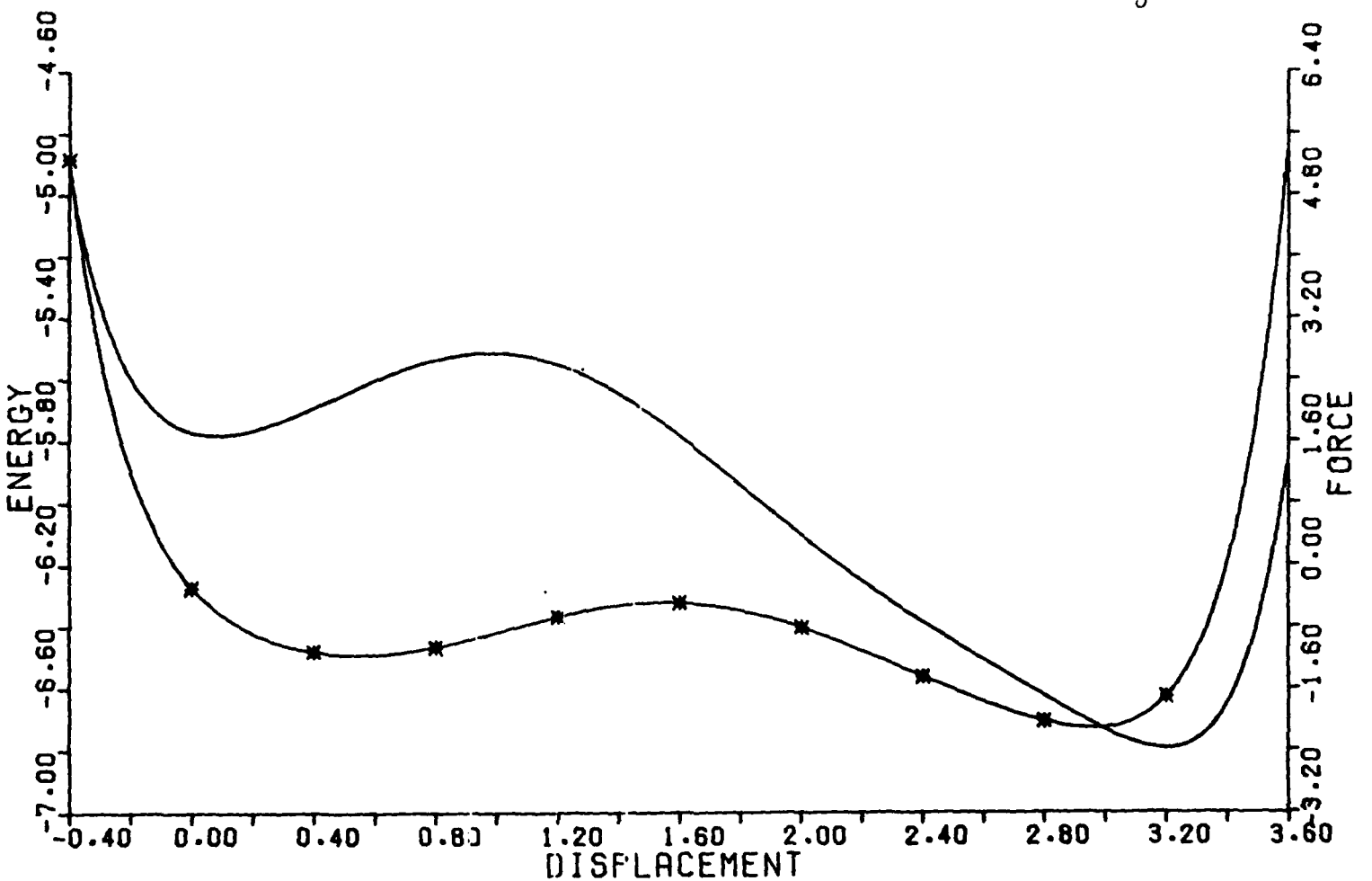
DISPLACEMENT

Fig 16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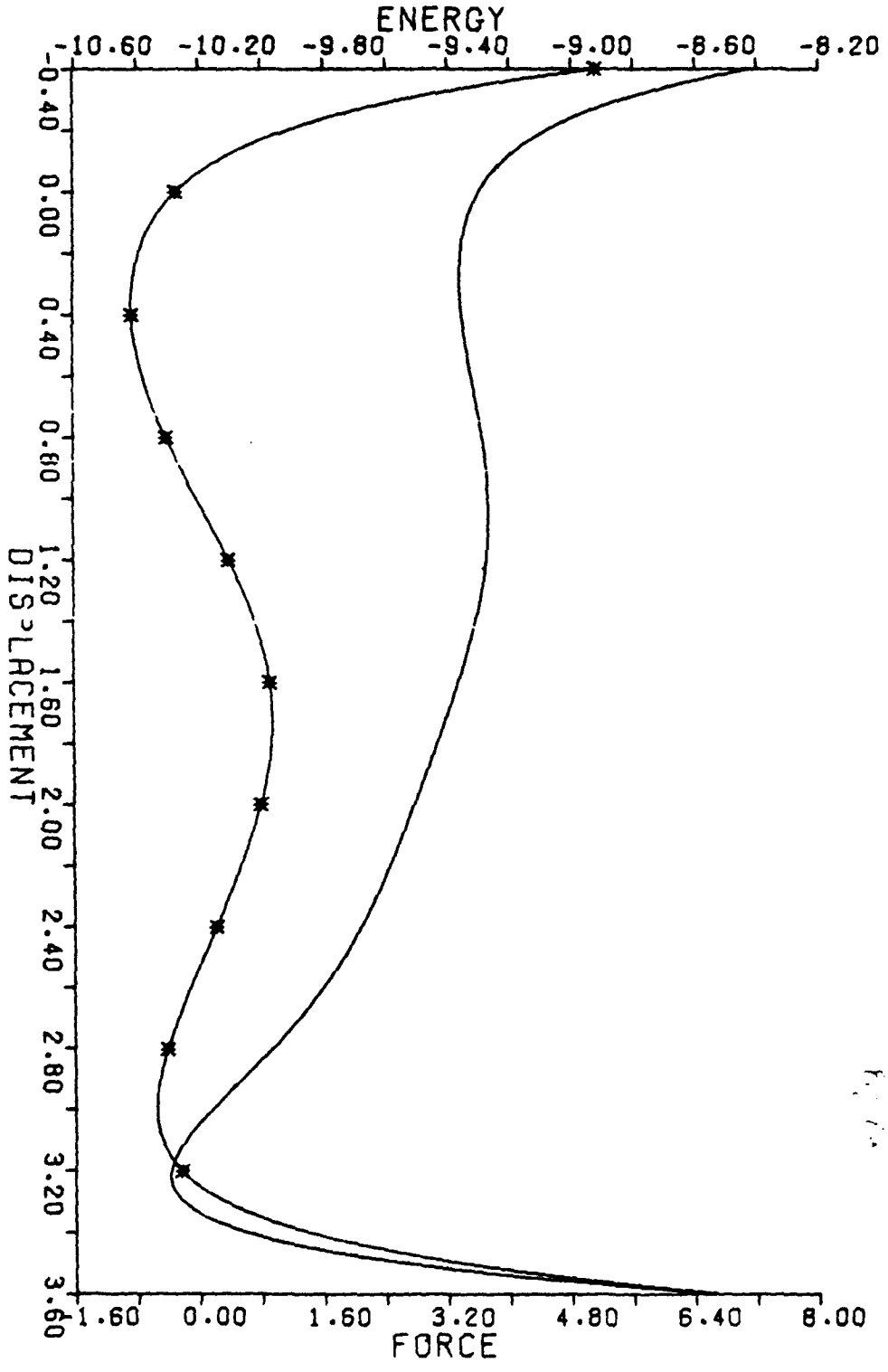
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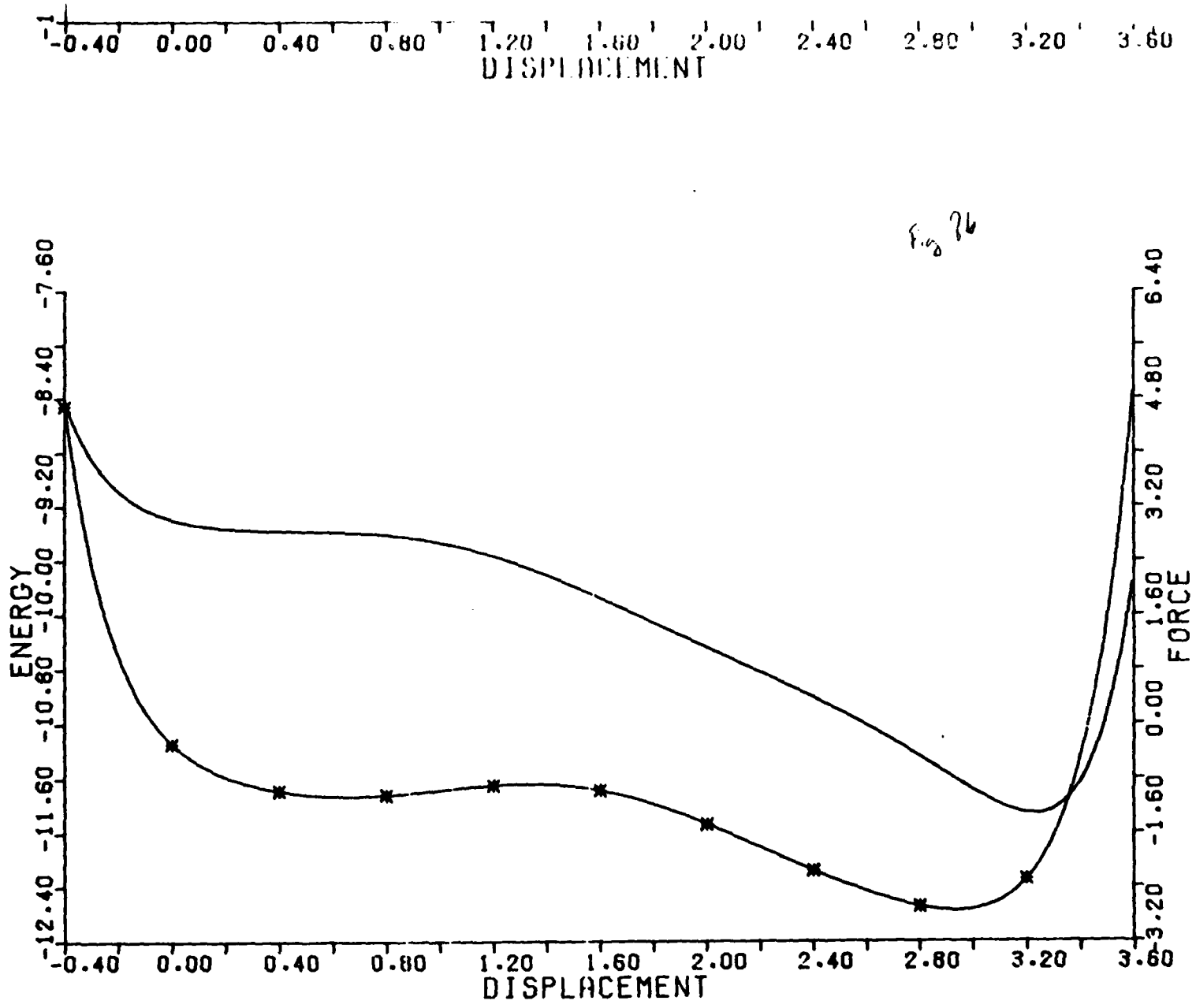
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DISPLACEMENT
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FORCE
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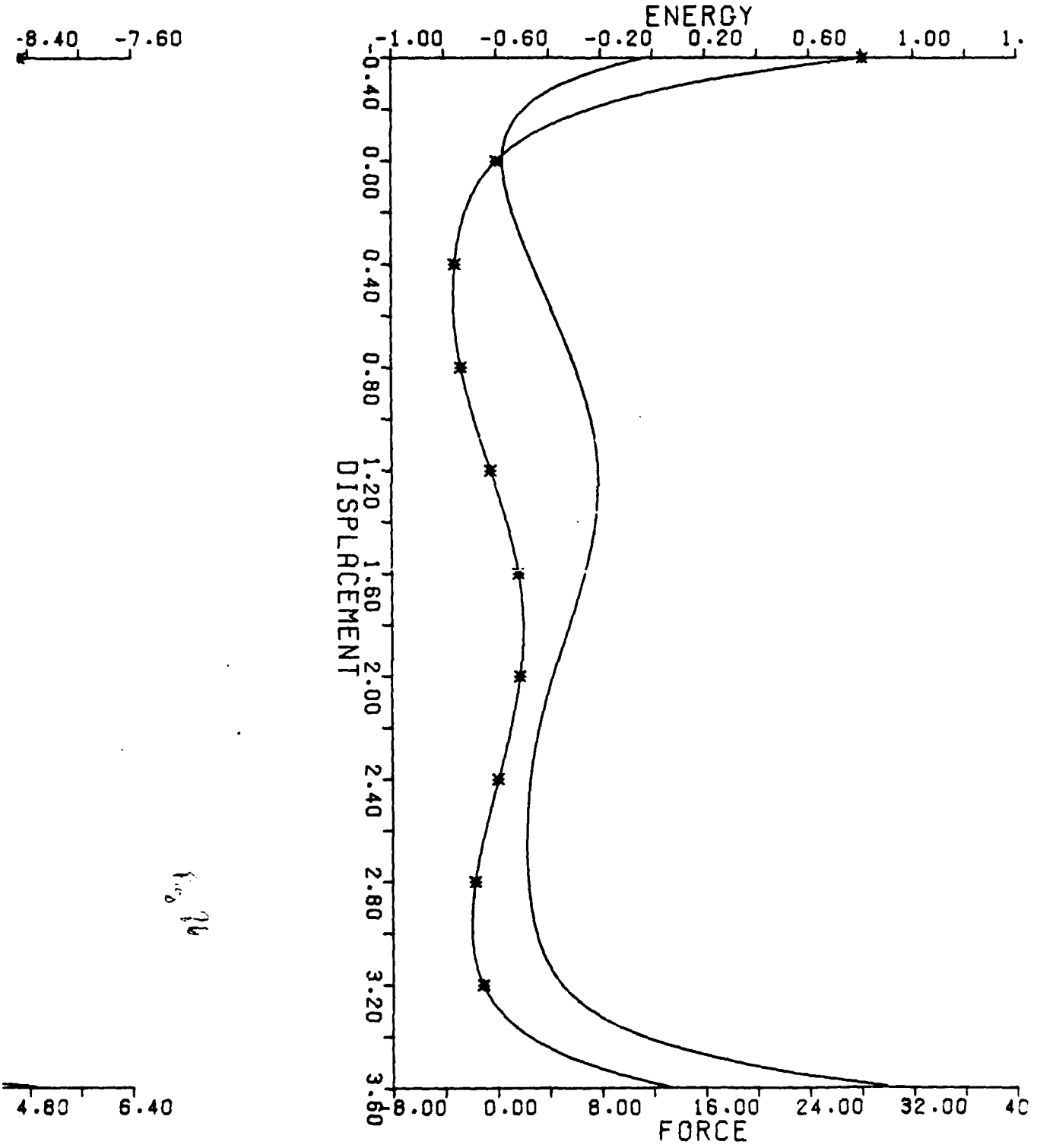
DISPLACEMENT

Fig 76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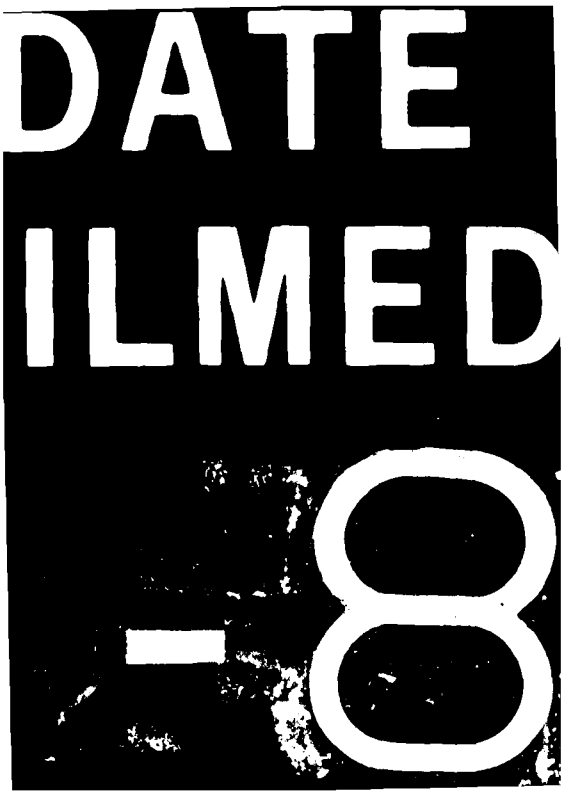
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